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by

T. A. Cahill, R. G. Flocchini, R. A. Eldred
and P. J. Feeney
Crocker Nuclear Laboratory Department of Physics
University of California, Davis, CA 95616

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Project Officer

Marc Pitchford
Advanced Monitoring Systems Division
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

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ABSTRACT

The design and operation of a 40-station network to sample atmospheric particles resulted in the collection, over a 2-year period from July 1979 to September 1981, of the data summarized in this report. The sampling stations were located in eight western states: Arizona, New Mexico, Utah, Colorado, Wyoming, Montana, North Dakota, and South Dakota. The 40 remote sites are regionally representative and are located on a nearly regular grid over the eight states.

Stacked Filter Unit samplers were chosen for their ease of operation, reliabilty, low-cost, and capability to provide samples segregated by size and compatible with elemental and gravimetric analyses techniques. The samplers collected both course (diameter between 15 and 2.5 microns) and fine (diameter less than 2.5 microns) particles. Collected twice weekly at each site, the samples covered 72-hour periods. Particle-induced x-ray emission (PIXE) analyses examined samples for elements greater in atomic weight than sodium. Samples were also analyzed gravimetrically for mass. Quality control procedures and an externally operated quality assurance audit program established the precision and accuracy of the resulting data.

Coarse particle concentrations are generally greater than the fine particle concentrations. The former are dominated by soil-related elements. Fine particles, representing about 30% of the total measured particle concentration, are of interest because of their impact on visibility and their capacity for long-range transport. Unlike coarse particle parameters, fine mass and fine sulfur concentrations are present in regional patterns on a scale that is easily seen by the monitoring network. The fine particles are comprised primarily of sulfates, soil-related materials, smoke, and materials too light in atomic weight to be seen by PIXE analysis (e.g. carbonaceous material and nitrates). Meteorological data implicate copper smelters and urban and industrial areas as the source of much of the fine particulate sulfur in the study area.

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CHAPTER 1

INTRODUCTION

The region of the western United States centered on the Great Basin and Rocky Mountain states includes about a quarter of the area of the contiguous 48 states but only about 8% of their population. It is an area rich in grandeur, with remarkable vistas, diverse and fragile ecological communities, and, consequently, a large proportion of U.S. national parks and monuments. The region also contains enormous energy and mineralogical resources, including deposits of coal, oil shale, and uranium, as well as ores of many nonferrous metals. The utilization of these resources may result in impacts upon air quality that threaten the natural condition of the region. In particular, visibility adequate to appreciate the scenery can be harmed even by air quality degradation that is modest in terms of existing health and welfare standards. Thus, visibility itself is now protected in many parks and monuments in the region.

Data on air quality taken routinely in the study region are largely irrelevant to the problem. Most existing air monitoring sites are in urban areas subject to local pollution sources. Little information is available from such sources on particulate size or composition, factors important both for evaluating natural and man-made contributions to particulate matter and their potential impacts on visibility. Existing monitoring data for particles are generated on a one-day-in-six protocol that hinders both statistical studies and correlations with meteorology. Finally, relatively few particulate monitoring sites exist in the area. There have been intensive research studies of air quality in the region, most notably the Visibility Impairment due to Sulfur Transport and Transformation (VISTTA) study funded by the U.S. Environmental Protection Agency (EPA). The valuable and detailed information from such studies is limited, however, to relatively short periods of time (about two weeks for VISTTA) and limited areas. Thus, they can provide little information on the entire area, seasonal factors, or baseline values for future trend analysis.

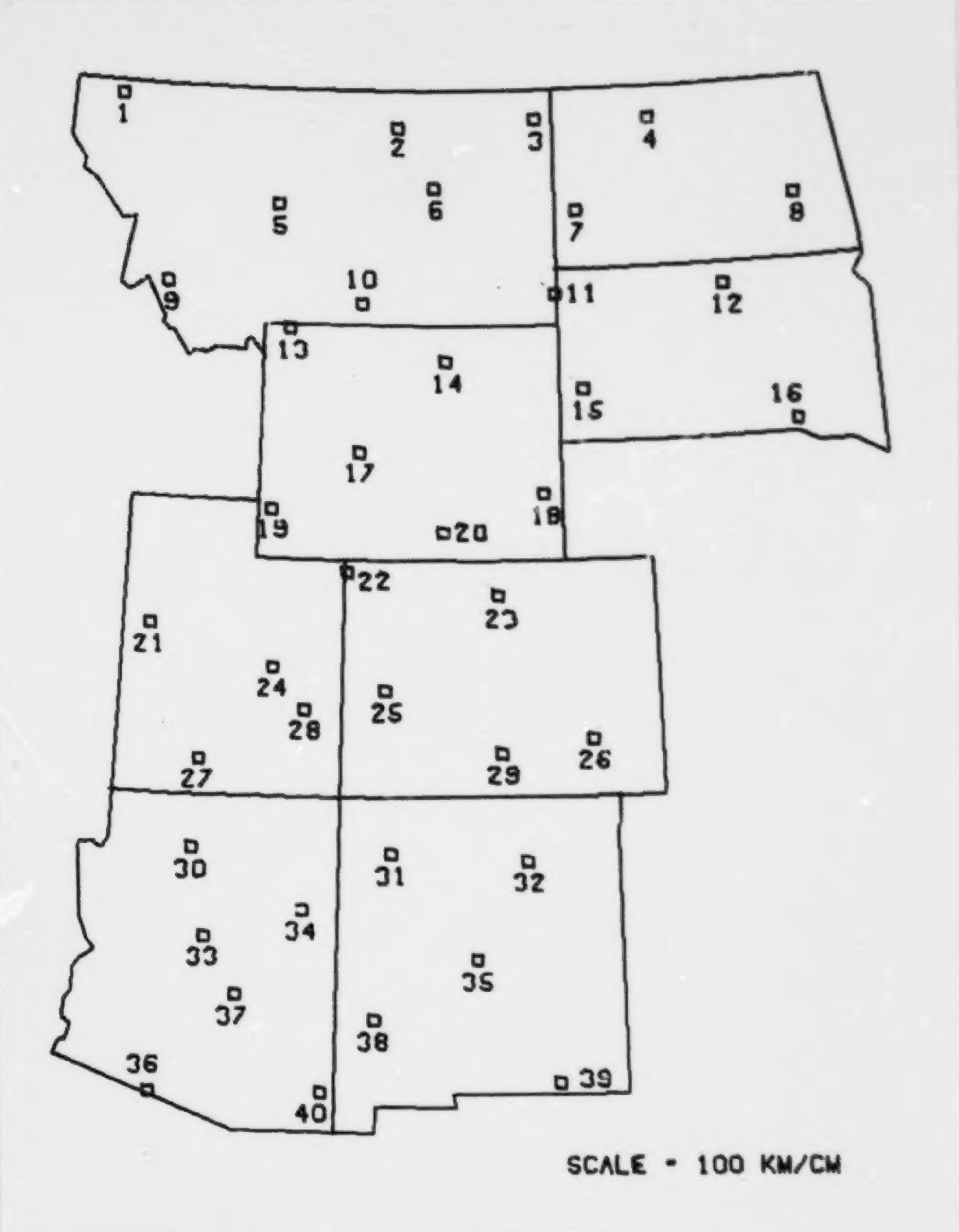
The three main purposes of a cooperative agreement between EPA and the University of California at Davis (UCD) were to: 1) develop sampling and analytical techniques suitable to the problem of nonurban air quality in the study region, 2) use these techniques to provide statistically sound data over the entire region for 27 months, and 3) begin the process of interpreting these results in terms of natural and man-made particles of local or transported origins. Each of these topics is described in this report.

Chapter 2 describes the sampling and analytical techniques developed and used in this program. Traditional air monitoring procedures for sampling and analysis could not be used in most cases due to the requirements for more detailed information than that available from such techniques, the very low values of most atmospheric contaminants, and the costs required to establish a large network at remote sites. Within the study area, anthropogenic sources tend to be isolated from each other or clustered in small subregions. Distances from such sources to remote receptor sites such as Class I air quality areas (international parks, national wilderness areas, and national memorial parks exceeding 5,000 acres; and national parks exceeding 6,000 acres) tend to be great, so that primary gaseous pollutants are usually immeasureably low by urban monitoring techniques. Thus, the study design included no routine measurements of primary gaseous pollutants. Particles, however, are known to be important throughout the region, both in terms of absolute concentrations, which could on occasion exceed all federal and state standards, and in terms of impacts such as visibility degradation. Particulate matter includes both natural and anthropogenic components, requiring both particulate size and chemical composition data to achieve source attributions. Particles also act as a major sink for gaseous pollutants and dominate transport of potentially toxic metals. Hence, the study was designed to emphasize particulate measurement on a regional scale.

Sampling sites were chosen so that as many sites as possible were located in Class I air quality areas. Sampling sites are shown in Figure 1.1 and listed in Table 1.1. Each site was chosen so as to minimize local sources of dust and avoid terrain effects such as atmospheric inversions associated with basins and valleys. Local operators were recruited and trained when possible, with the assistance of public agencies, especially the National Park Service. Exchange of samples between field locations and UCD was accomplished via the U.S. Postal Service and United Parcel Service using UCD-designed sealed filter cassettes that eliminated handling of filters by sampling station personnel. Samples were collected in over 91% of all possible sampling periods, often under very difficult conditions of access and weather. In order to obtain accurate mean values for particulate concentration, the network operated on a cycle of two 72-hour periods per week, 52 weeks per year, over three summers and two winters in the study. This allowed coverage of 86% of all time periods, versus the 17% in traditional one-day-in-six particulate sampling. It also allowed the program to maintain a weekend-weekday separation of time periods, while the 72-hour duration still allowed for analysis of the effect of synopic meteorological changes on particulate concentrations.

Since the role of particulate size is of great importance in pollutant transport, source identification, and visibility impacts, samples were collected in two particulate size categories: fine particles below 2.5 micrometer (μm) in aerodynamic diameter and coarse particles between 2.5 μm and 15 μm. A 15-μm size selective inlet baffled to reduce the effect of wind on the upper cut-off points was developed and deployed in this study.

Analysis of the samples collected on the coarse and fine filters of the dichotomous stacked filter unit (SFU) and virtual impactor (VI) samplers was carried out at UCD. Gravimetric analysis of mass was accomplished on all samples and new techniques were developed and published to allow us to handle the extremely low mass levels encountered in the study. All samples were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SCALE = 100 KM/CM

Figure 1.1. Western particulate characterization study sampling sites.

TABLE 1.1. WESTERN PARTICULATE CHARACTERIZATION STUDY SAMPLING SITES

		Longitude		Latitude		
		Deg.	Min.	Deg.	Min.	Elevation
1.	Murphy Lake, MT	114	53	48	45	3100
2.	Malta Airport, MT	107	54	48	21	2280
3.	Medicine Lake NWR, MT	104	27	48	29	2000
4.	Upper Souris NWR, ND	101	35	48	27	1700
5.	Belt Creek Ranger Station, MT	110	49	47	02	5800
6.	Jordan Airport, MT	106	58	47	20	2638
7.	Theodore Roosevelt NMP, ND	103	30	46	56	2340
8.	Bald Hill Dam, ND	98	05	47	02	1300
9.	Big Hole Valley, MT	113	24	45	22	6060
10.	Bluewater Fish Hatchery, MT	108	42	45	21	3700
11.	Charlie Odell's Ranch, MT	104	04	45	30	3500
12.	Lake Hiddenwood State Park, Sd	100	00	45	34	1784
13.	Yellowstone NP, WY	110	25	44	55	6270
14.	Buffalo Airport, WY	106	43	44	23	4950
15.	Mount Rushmore NM, SD	103	27	43	53	4820
16.	Lake Andes NWR, SD	98	35	43	20	1442
17.	Lander Airport, WY	108	45	42	50	5400
18.	Fort Laramie NHS, WY	104	30	42	07	4260
19.	Fossil Butte NM, WY	110	45	41	51	6900
20.	Saratoga, WY	106	47	41	28	7000
21.	Fish Springs NWR, UT	113	21	39	50	4300
22.	Brown's Park NWR, CO	108	58	40	48	5500
23.	Rocky Mountain NP, CO	105	34	40	22	7900
24.	Cedar Mountain, UT	110	37	39	10	7665
25.	Delta County airport, CO	108	04	38	47	5166
26.	1st Combat Evaluation Group, Strategic Air Command, CO	103	25	38	04	4238
27.	Bryce Canyon NP, UT	112	11	37	34	8000
28.	Canyonlands NP, UT	109	50	38	27	5925
29.	Great Sand dunes NM, CO	105	31	37	44	8225
30.	Grand Canyon NP, AZ	112	10	36	04	6800
31.	Chaco Canyon NM, NM	107	55	36	02	6385
32.	Fort Union NM, NM	105	01	35	55	6700
33.	Montezuma Castel NM, AZ	111	50	34	36	3200
34.	Petrified Forest NP, AZ	109	47	35	05	5820
35.	Grand Quivira NM, NM	106	06	34	16	6620
36.	Organ Pipe Cactus NM, AZ	112	48	31	57	1650
37.	Tonto NM, AZ	111	08	33	38	2600
38.	Gila Cliff Dwelling NM, NM	108	14	33	14	5700
39.	Carlsbad Caverns NP, NM	104	26	32	10	4400
40.	Fort Bowie NHS, AZ	109	29	32	08	4500

NWR -- National Wildlife Refuge
NMP -- National Memorial Park
NP -- National Park
NM -- National Monument
NHS -- National Historic Site

analyzed by particle induced x-ray emission (PIXE) for elements sodium and heavier.

Over 17,000 multi-elemental analyses were made of the 14,920 valid, analyzable samples included in the final data set, for about 440,000 observed values or upper detection limits of individual elements. Other techniques such as x-ray fluorescence (XRF) and forward alpha scattering techniques (FAST) were used to provide additional information on selected samples. The entire sampling and analysis program was under an independent quality assurance program designed to document both accuracy and precision via flow and system audits, and analytical intercomparisons.

Chapter 3 presents statistical summaries of the data from the network. These data are broken down into coarse and fine particle size fractions, separated by the 2.5 μm cut point of the samplers. Coarse particle concentrations vary from site to site, and no consistency can be found across the network. Since these particles have little ability to travel long distances, they originate from local sources in most cases. High intercorrelations among the traditionally classified soil-derived particle elements Al, Si, K, Ca, Ti, Mn, and Fe, and high correlations between these soil tracers and coarse mass, establish the dominant role of soils in coarse particles. This is confirmed by the compositional similarity between resuspended soil samples taken at all network sites and the coarse particles present at the same site. Coarse mass dominates the total mass of all particles between 0 and 15 microns diameter.

Fine particle concentrations are distributed more uniformly across the network, as might be expected due to the ability of particles smaller than 2.5 μm to travel long distances. Fine particulate mass is usually dominated by sulfur containing particles, but a large fraction of the mass is composed of elements lighter than sodium and thus unobservable by normal x-ray based techniques such as PIXE or XRF. Strong seasonal and regional patterns are observed, aiding in allocation of fine particles to sources both local and distant. A major impact of smoke upon fine particle concentration was discovered, through use of the fine particle K tracer in the smoke. The 1980 copper smelter strike provided data on the role that smelters play in fine particles in the southern 4 states of the network.

An annotated bibliography shows the progress made on interpretation of the network data. A list of all publications resulting from the program, in terms of development of sampling and analytical techniques, network design, ancillary studies and understanding of particles and their sources, is given. A fuller accounting of interpretitive efforts is beyond the scope of this report; however, data (on magnetic tape and as printed summaries) from the network are available to and being used by the research and regulatory communities.

CHAPTER 2

SAMPLE COLLECTION AND ANALYSIS

SAMPLING SITES

Site Location

The first step in analyzing ambient air quality over the 8-state region was the establishment of a nonurban sampling network. Forty sampling sites were chosen for the Western Particulate Characterization Study and placed in a relatively uniform grid over the region with as many sites as possible in Class I areas. (Site locations are shown in Figure 1.1 and listed in Table 1.1.) A local station operator was responsible for changing the filtering media supplied by the UCD.

Site Criteria

Each site was visited by a member of the site selection team to determine suitability and accessibility. Possible local sources, local climatological conditions, and power requirements were evaluated. Each location had to meet a set of general site criteria, and the sampler position had to meet a set of specific site criteria.

General Site Criteria--

The site had to be:

1. Remote and regionally representative (for a distance of approximately 100 KM). Valleys were avoided if possible as was proximity to local sources.
2. Located with existing pollutant and meteorological monitoring equipment when possible without compromising the first criteria.
3. Easily accessible throughout the year and maintained by responsible persons.
4. Reasonably secure.
5. Able to supply 110 V 60 cycle power at not less than 600 watts.

Specific Site Criteria--

1. The intake of the sampler was from 2 meters to 15 meters above the

ground. The intake of the sampler is about 0.5 meters above its base. In cases where the roof of a building was a possible site, the intake was located approximately two meters above the roof. No roof sites were considered when furnace or incinerator flues were nearby.

2. The distance from the site to buildings, trees, or other obstructions was at least twice the height of the obstruction above the sampler.

3. The sampler was positioned away from parking lots, paved roads where traffic loads were greater than 30 vehicles per hour, and dirt roads that were a possible source of resuspended dust.

A detailed description of the sites selected for this network, including a site description, a map, and a set of photographs, is available in Flocchini et al. (1981).

SAMPLING EQUIPMENT

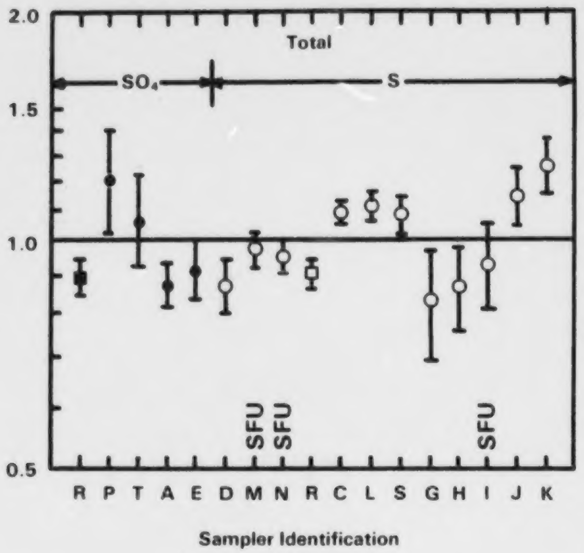
Stacked Filter Unit

The stacked filter unit (SFU) is a two-stage sampler in which size segregation is provided by the collection efficiency of 8-μm pore size Nuclepore pre-coated membrane filter. The sampler was designed so that the fine stage collected respirable particles (less than 2.5 μm diameter), while the sum of the two stages collected inhalable particles (less than 15 μm diameter). The SFU was used at all forty sites.

Early versions of the SFU were tested in the EPA-DOE Charleston Sampler Intercomparison (Camp et al., 1978) by both the EPA (Research Triangle Park) and UCD. Results for an important pollutant species, sulfur/sulfate, are shown in Figure 2.1. In general SFU's were equivalent in accuracy and precision to other units for predominantly fine particles. These tests did show some enhancement of fine soil particles in the SFU's, an effect corrected in later units by coating the first filter. Successful performance of SFU's at Charleston led to their further development and their use in this study as the primary particulate sampler. This choice was based upon the simplicity and reliability of the SFU design, their ability to withstand severe meteorological conditions, without any shelter whatsoever, and their suitability for use of filter cassettes that eliminated any direct filter handling at the sites. Forty units of the revised UCD design were built by AeroVironment Inc.

As illustrated in Figure 2.2, the air enters the SFU through an intake manifold with a 50% capture of 15-μm aerodynamic diameter particles. The intake characteristics were validated by wind tunnel tests performed in June 1980 at Texas A M. The first stage uses an 8-μm Nuclepore filter. The collection efficiency for this filter at a flow rate of 10 liters per minute (lpm) is shown in Figure 2.3 (Cahill et.al, 1978 b). This curve will shift to the right as the pore size increases or as the flow rate decreases. Shown for comparison is the collection efficiency of the upper respiratory tract and the bimodal distribution of particles in typical urban aerosols.

The 50% capture diameter, or cutpoint, is the particle diameter at which 50% of the particles are collected by the filter. The variation of the cutpoint as a function of flow rate (expressed in terms of face velocity) is shown in



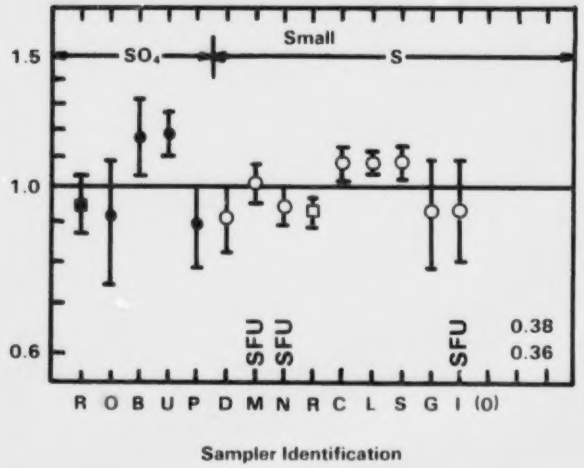


Figure 2.1. Sulfur/sulfate results from Charleston study. Average and standard deviations of the ratio of a sampler's result to the average of all results for 16 sample periods for total (all sizes) and fine particle sulfur/ sulfate.

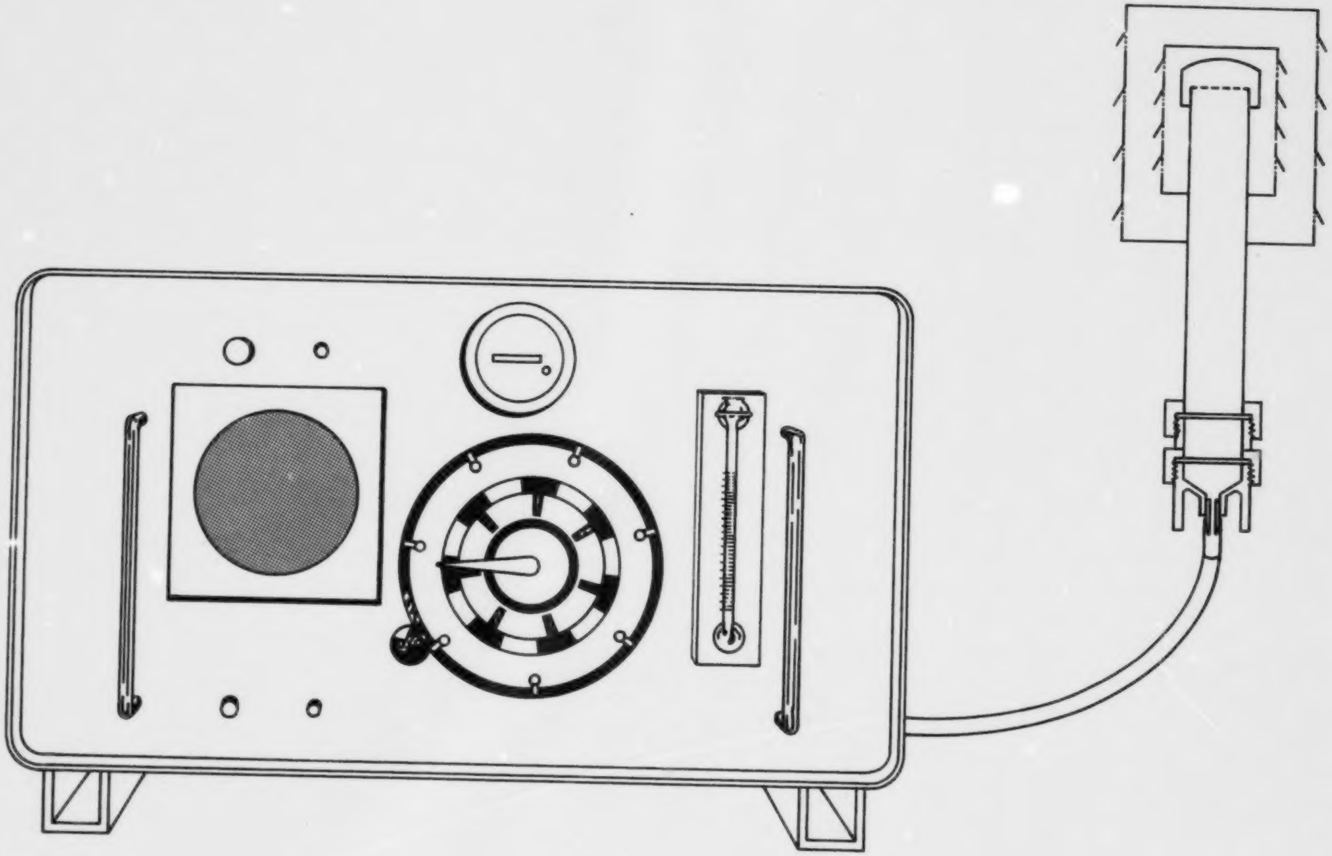


Figure 2.2. Stacked filter unit.

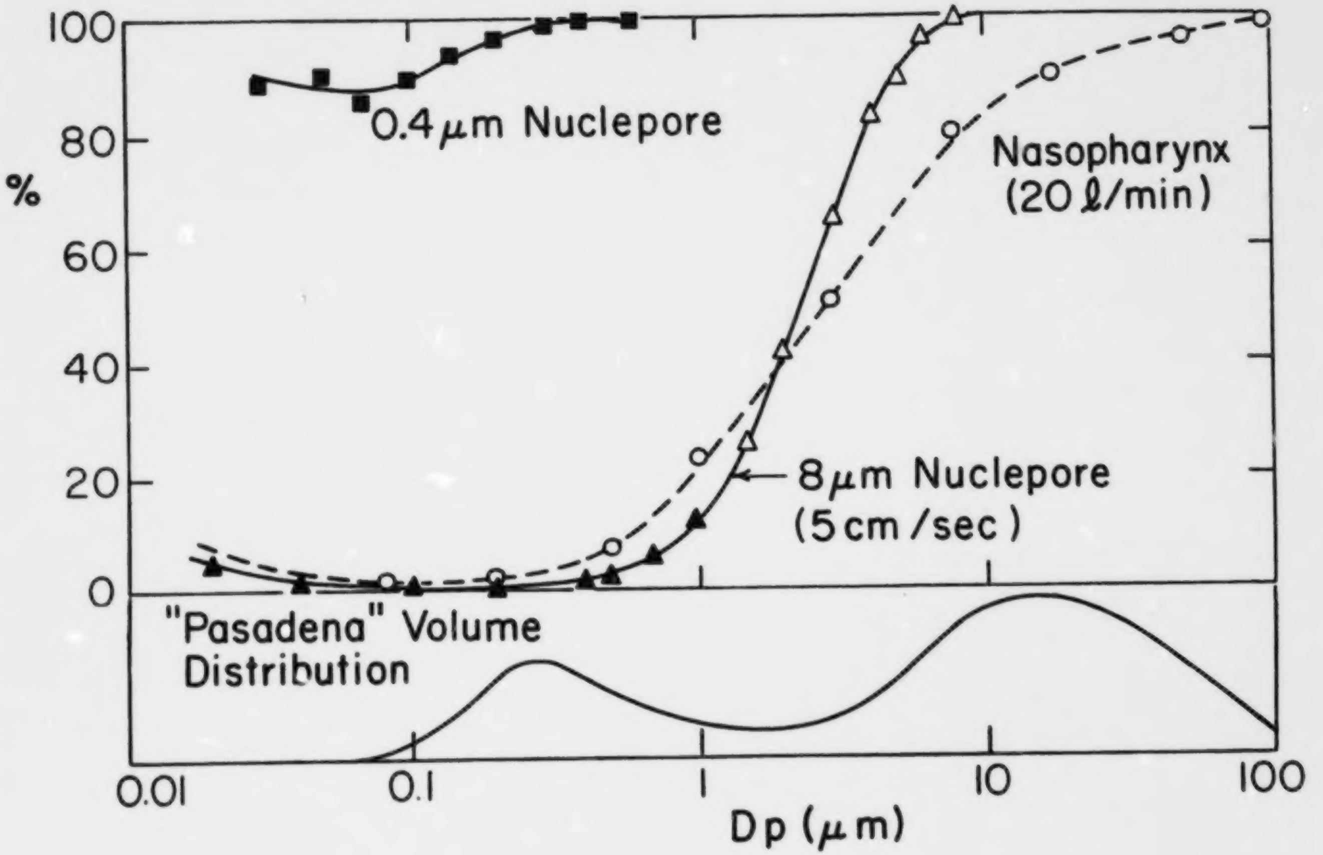


Figure 2.3. Aerosol collection efficiency.

Figure 2.4 for several filter pore sizes. These curves indicate that the 50% capture diameter does not change significantly at low flow rates.

Nuclepore filters are produced by irradiating a polycarbonate film with charged particles from a nuclear reactor. The tracks left by the particles are preferentially etched into uniform, cylindrical pores. By controlling the time length of the etching process, a specific pore diameter is produced. The rated pore size specifies the maximum pore diameter. The variation in the 50% capture diameter as a function of pore diameter is shown in Figure 2.5. At 10 lpm the variation is nearly linear. The variation in pore size produces a significant change in the cutpoint, whereas a change in flow rate does not. This problem was eliminated by using a single batch of filters for the entire program. The filters were selected and tested for a cutpoint of 2.5 µm, and were pre-analyzed for elemental purity.

In order to minimize passage of dry particles onto the fine filter via particle bounce off, the 8-µm filters were coated with a thin, 5 microgram per square meter ($\mu g/m^2$), layer of Apiezon L grease. The coating is hydrophobic, and mass values change little even after exposure to vacuum. Extensive tests of coated and uncoated filter at UCD (Figure 2.6) and by the California Department of Public Health with laboratory aerosols indicate a negligible change in capture diameter for wet aerosols and greatly improved collection efficiently for dry aerosols (John, 1980).

Because the collection efficiency of the 8-µm Nuclepore filter does not provide an infinitely sharp cut-off at 2.5 µm, particles near this diameter may be collected on the wrong stage. The magnitude of this effect was calculated from the collection efficiency curve and an assumed ambient distribution of particle sizes for the elemental species. For this calculation, a series of ambient size distributions were used, each had an accumulation mode curve with a peak at 0.2 µm and dropped to zero at 6 µm, and a coarse mode curve beginning at 0.4 µm and reaching a maximum at 12 µm. Table 2.1 shows the distribution of masses (percent of mass on fine stage) for the SFU sampler and the corresponding "true" distribution as would be realized by an idealized sampler with infinitely sharp cut-off at 2.5 µm. For predominately coarse particles, such as soil-derived particles, the SFU coarse concentrations are smaller and the fine concentrations are larger than the corresponding true concentrations. For the entire network, 19% of the mass of soil-derived elements was on the fine stage. From the table, this indicates that 17% of the soil mass was truly smaller than 2.5 µm. Thus coarse concentrations were 2% too small (81/83=.98), while the fine concentrations were 12% too large (19/17=1.12). For predominately fine particles, such as sulfate, the SFU fine concentrations are smaller and the coarse concentrations are larger than the corresponding true concentrations. For the network, 88% of the sulfur mass was on the fine stage, corresponding to a true distribution for sulfur of 90% smaller than 2.5 µm. Thus 17% of the sulfur on the coarse stage was actually smaller than 2.5 µm. Supporting this analysis, the network data indicate that the coarse-stage sulfur concentrations are not dominated by incorrectly sized fine sulfur, as there is a low correlation between coarse and fine sulfur concentrations.

The purpose of the fine-stage filter is to collect all particles that pass through the coarse filter. Any highly retentive filter that delivers a sample

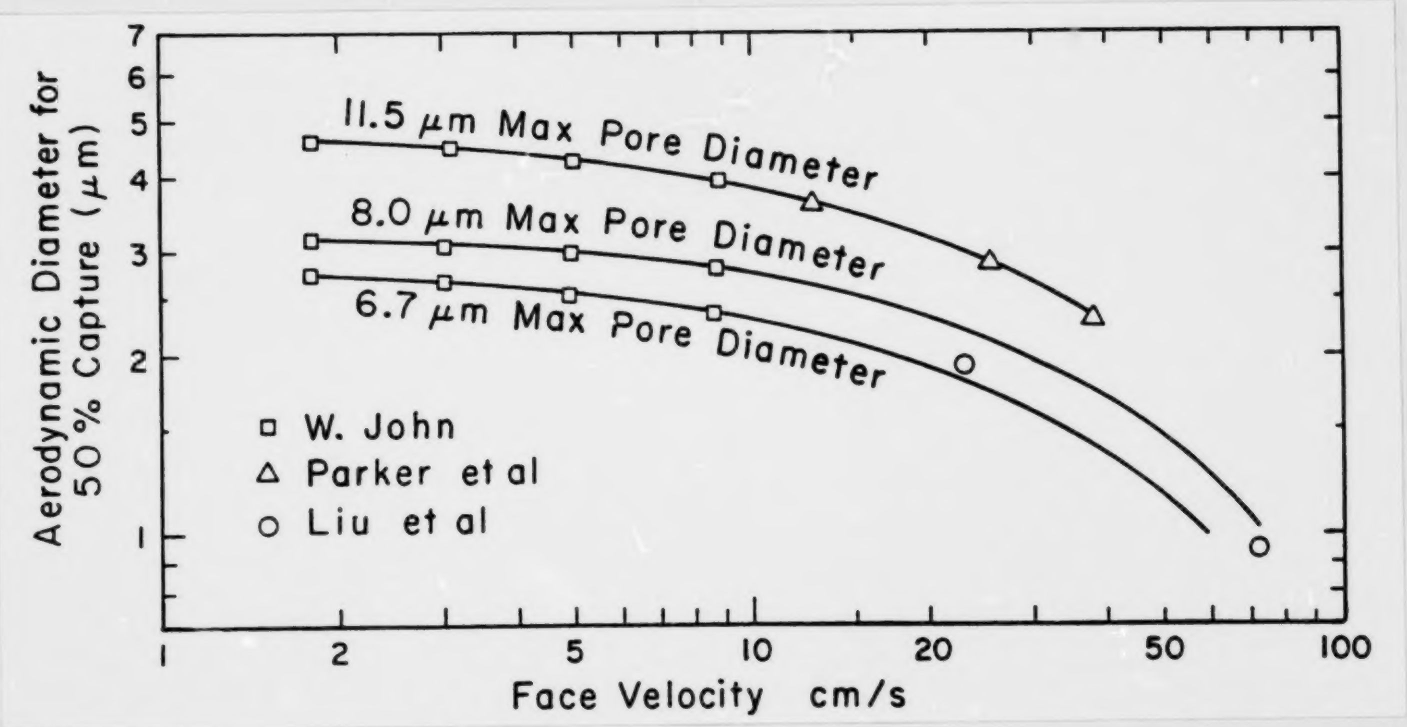


Figure 2.4. Variation of aerodynamic diameter as a function of face velocity.

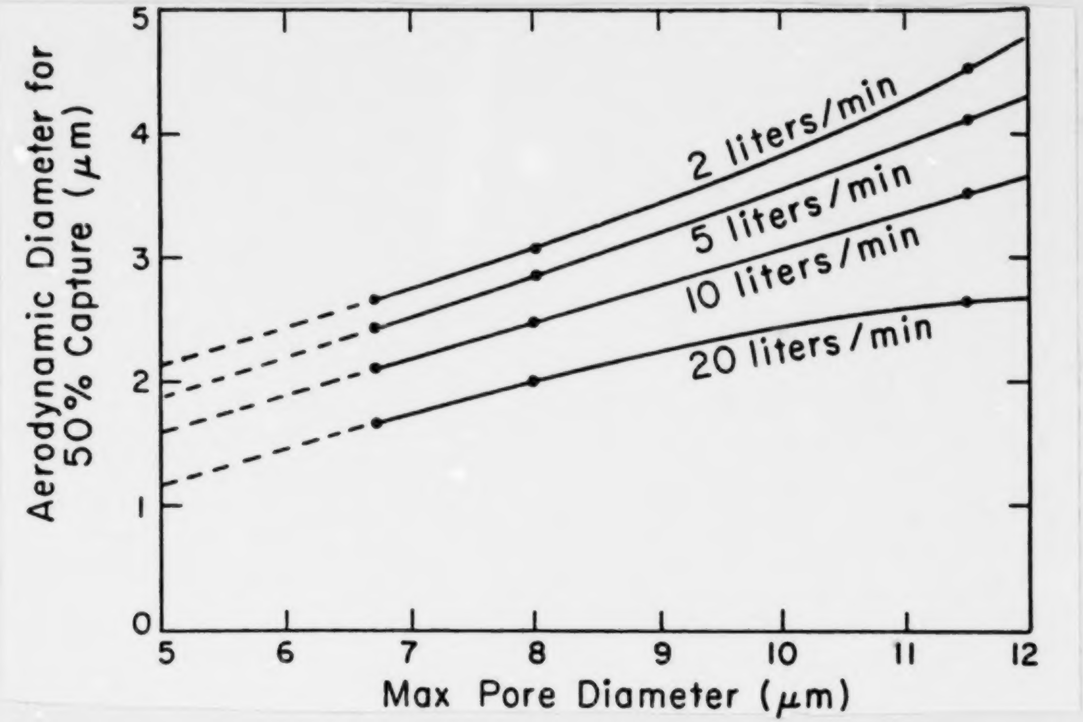


Figure 2.5. Variation of aerodynamic diameter as a function of pore diameter.

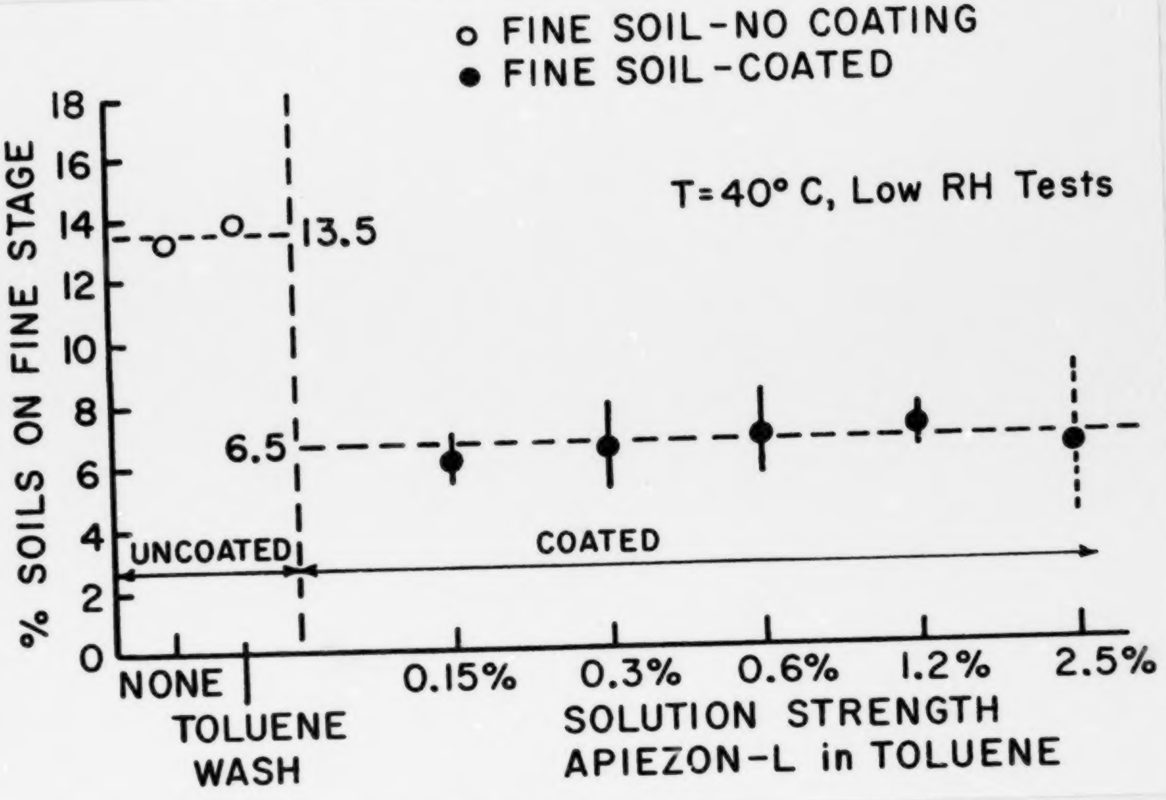


Figure 2.6. Effect of coatings on soil bounce-through to fine filter.

TABLE 2.1. PERCENT OF MASS ON FINE STAGE

SFU	Infinitely Sharp 2.5 μm
15%	12%
19%	17% (soils)
22%	20%
32%	30%
41%	40%
50%	50%
60%	60%
69%	70%
79%	80%
88%	90% (sulfur)
97%	99%

suitable for analysis of mass and composition may be used. The filter chosen for this study was a 0.3-μm Nuclepore custom-made, high pore density filter. This filter has an areal density of 0.8 mg/cm^2, is highly efficient (99%) in the region of interest, and is easily analyzed by particle induced x-ray emission (PIXE). All filter batches, both coarse and fine, were analyzed for elemental contamination. A trace amount of bromine was detected on about 6% of the coarse filters.

Air flow was maintained by a 1/8 horsepower diaphragm pump with a volumetric flow controller. A flow rate of 10 lpm was regulated within ±5 percent to a pressure drop of 35 cm Hg across the filters and was monitored by the system's rotameter. The sample flow rate was calibrated using an orifice meter with magnehelic gauge when the samplers were purchased and again any time the rotameter or pump was replaced. The orifice meter was calibrated at UCD with a spirometer. A calibration curve for the orifice was obtained in the form

$$\log(Q) = a_1 + a_0 \log(P)$$

where Q is the flow rate as measured by the spirometer and P is the pressure drop across the orifice in inches of water.

When the units were first placed in the field, initial calibration curves for the samplers' rotometers were made. A spirometer-calibrated orifice was attached to the sampler inlet so that the sample flow passed through the orifice. Measurements were taken for several flow rates, a plot of the rotameter reading versus flow rate was constructed and a least squares straight line determined for it. This regression line was used as the calibration curve for each SFU tested after adjusting it for site elevation.

The flow rate was corrected for site elevation using the equation

$$Q' = Q\,(P_o/P_s)^{0.5}$$

where Q' is the indicated flow rate, obtained from the calibration curve, P_o is the pressure at Davis, CA (assumed to be 760 mmHg), and P_s is the pressure at the site. Table 2.2 lists the calibration curve constants corrected for site elevation for each site. In addition to the initial calibration, each sampler was spot checked periodically with an orifice meter by the site operator. Most of the sites were recalibrated by UCD personnel once each year.

A 7-day timer/controller turned the pump on and off at preset times, while the elapsed timer provided an accurate account of sampling duration. The sampler's elapsed time meter was checked in the laboratory and in the field every twelve months against a timepiece of known accuracy. A gain or loss of more than five minutes in twenty-four hours warranted replacement. The calibration for the on-off timer was monitored routinely by checking the elapsed time reported from the field. If it varied more than 180 minutes from 4320 with no explanation from the operator, the operator was requested to check it.

Before the samplers were taken to the sites each was tested for pump reliability and time accuracy. They were flow calibrated and tested for

TABLE 2.2. CALIBRATION CURVE REGRESSION CONSTANTS* INCLUDING ALTITUDE CORRECTION (October 20, 1980)

Site	a	b	Site	a	b
1	0.059	0.957	21	-0.299	0.998
2	1.056	0.714	22	0.841	0.820
3	-0.036	0.859	23	0.524	1.014
4	0.087	0.893	24	-0.114	0.962
5	-0.054	1.016	25	0.756	0.902
6	0.160	0.878	26	0.559	1.004
7	-0.066	0.827	27	-0.087	1.022
8	-0.590	0.917	28	-0.254	1.044
9	-0.260	0.970	29	0.000	1.058
10	0.851	0.967	30	-0.007	1.000
11	0.427	0.914	31	0.393	0.961
12	0.644	0.745	32	-0.061	1.110
13	0.248	1.023	33	-0.428	0.970
14	-1.183	0.814	34	0.220	0.895
15	0.968	0.964	35	-0.061	1.108
16	0.209	0.765	36	0.000	0.935
17	0.058	1.026	37	0.700	0.907
18	-0.280	0.958	38	0.059	1.032
19	1.721	0.916	39	0.000	0.983
20	0.745	0.890	40	0.000	0.986

*Q_c = $a + b\, Q_m$ Q_c = Correct flow Rate Q_m = Measured Flow Rate (rotameter)

intercomparability. Results of side-by-side tests for all units using ambient aerosols gave the following precision (one standard deviation) values:

Stage 1 (coarse)	10%
Stage 2 (fine)	7%
Total (sum of 1 + 2)	7%

Units were shipped to field sites, and installed by UCD personnel. Local operators were taught proper operating procedures.

Sampling began at some sites in August 1979, and the network was fully operational by October 1979. Sampling ended on October 1, 1981. There were approximately 8200 sampling periods for all the sites or approximately 16,400 individual samples possible. Nine percent of these were not delivered to UCD due to a malfunction of the unit or to the inability of the operator to get to the sampler to change the filter. Two percent of the samples were discarded after analysis. Eighty-nine percent were received, analyzed and included in data. The distribution of valid analyzed samples is shown for each site in Figure 2.7.

Other Sampling Instruments

While the SFU's provided the bulk of the data for the network, a number of other sampling instruments were employed. The reasons for this were varied; the need for side-by-side intercomparisons for quality assurance purposes, the need for more size information, the need for additional time resolutions, and support for intensive studies carried on within the network region during this program such as the EPA VISTTA program. Details of these units and their use are given in Appendix B.

SAMPLE ANALYSIS

Methods

Particle-Induced X-ray Emission (PIXE)--

A diagram of the analytical system developed by the UCD is given in Figure 2.8. A 4.5 MeV proton beam from the 76" isochronous cyclotron passes through remotely readable graphite collimators and impinges on a thin target which is mounted at an angle of 45 degrees to the incoming beam. The target changing mechanism operates under real-time computer control.

The beam spot is made uniform over the target and is collected by a Faraday cup which integrates to a precision of approximately 2% to give the total charge Q that passes through the sample. X-rays pass through an active filter and a 25 μm Be window and are converted into electrical pulses by a 30 mm^2 x 3 mm thick liquid nitrogen cooled Si(Li) detector and associated pulsed optical feedback circuitry. Data are accumulated in a PDP 15/40 computer.

The number of characteristic x-rays, N_Z, corresponding to some transition of element Z was correlated with the areal density (ρt) of the element present in the sample by $N_Z = AQ(\rho t)$ where A is determined through the use of gravimetric

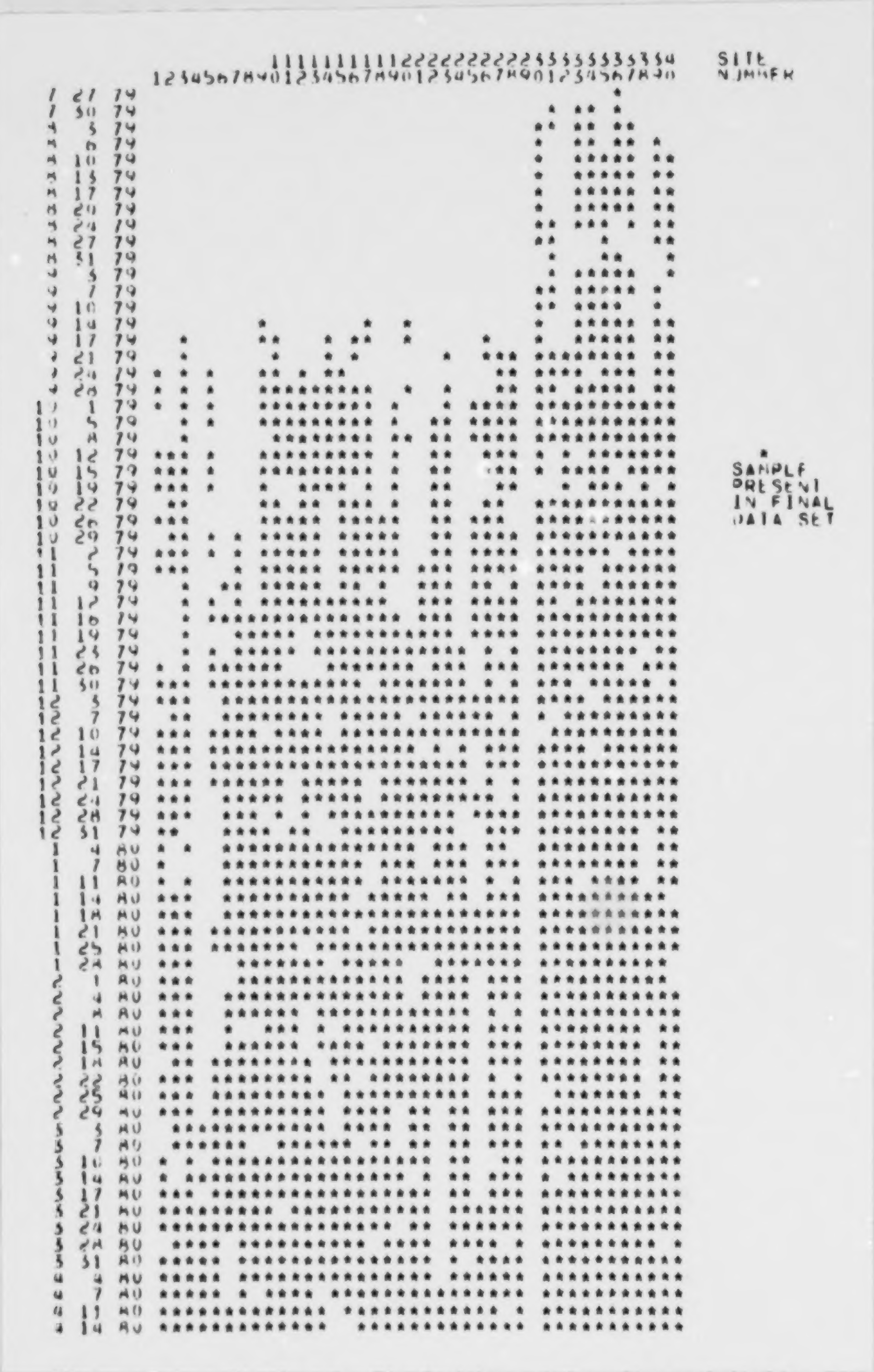


Figure 2.7. Samples in final data set by site and start date 7/27/79 to 9/28/81.

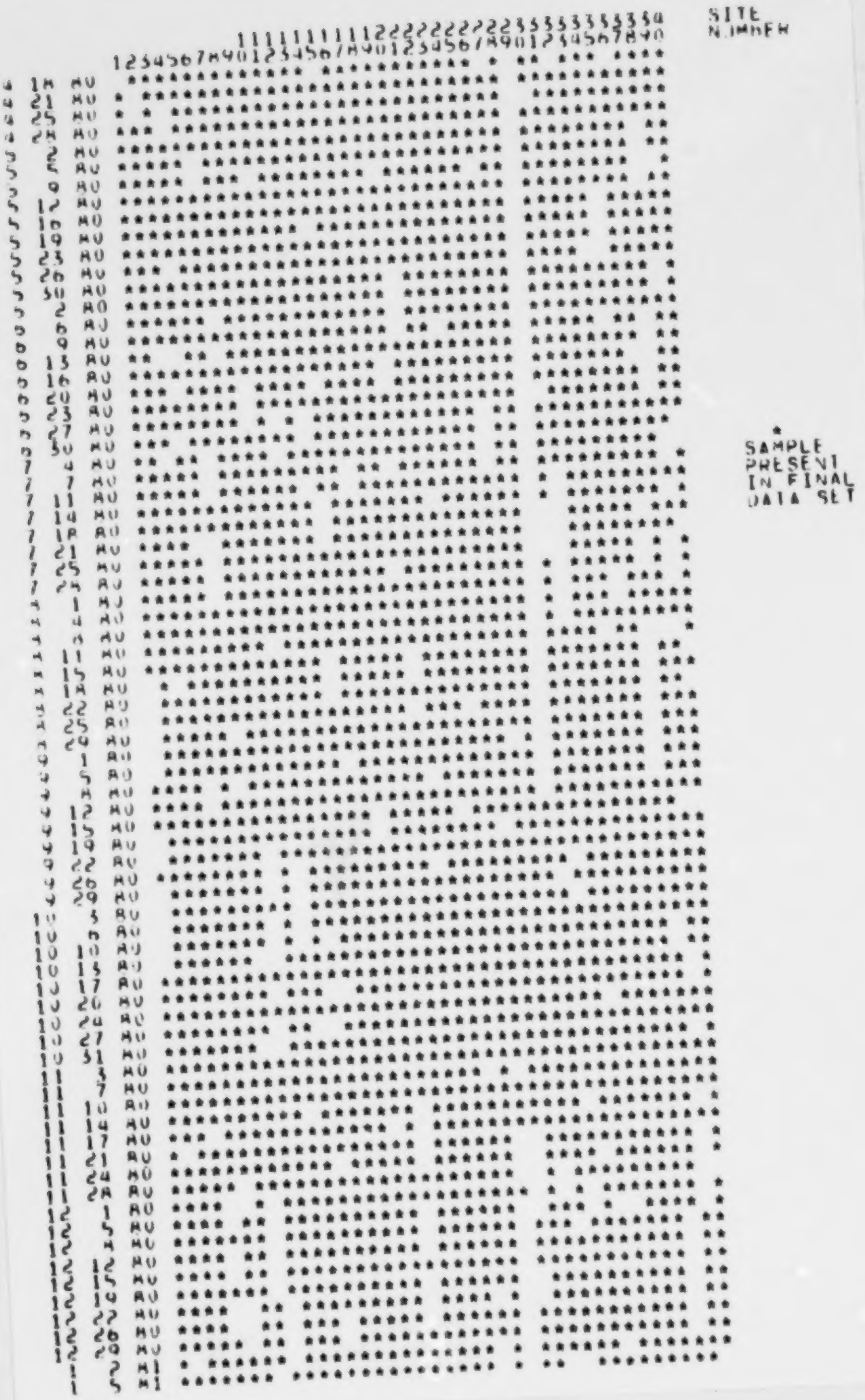

SITE NUMBER
1234567890123456789012345678901234567890
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Figure 2.7. (Continued).

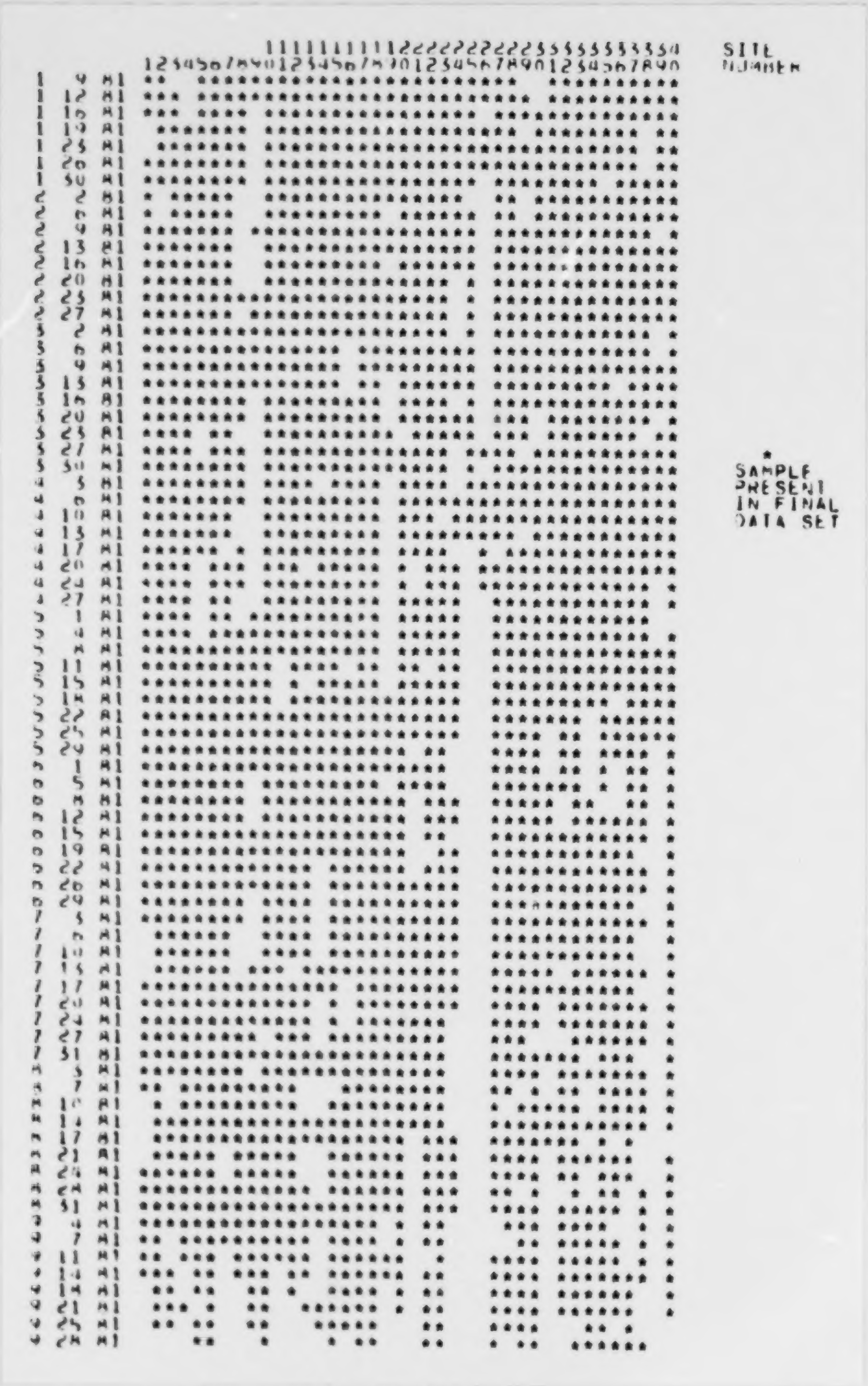

Figure 2.7. (Continued).

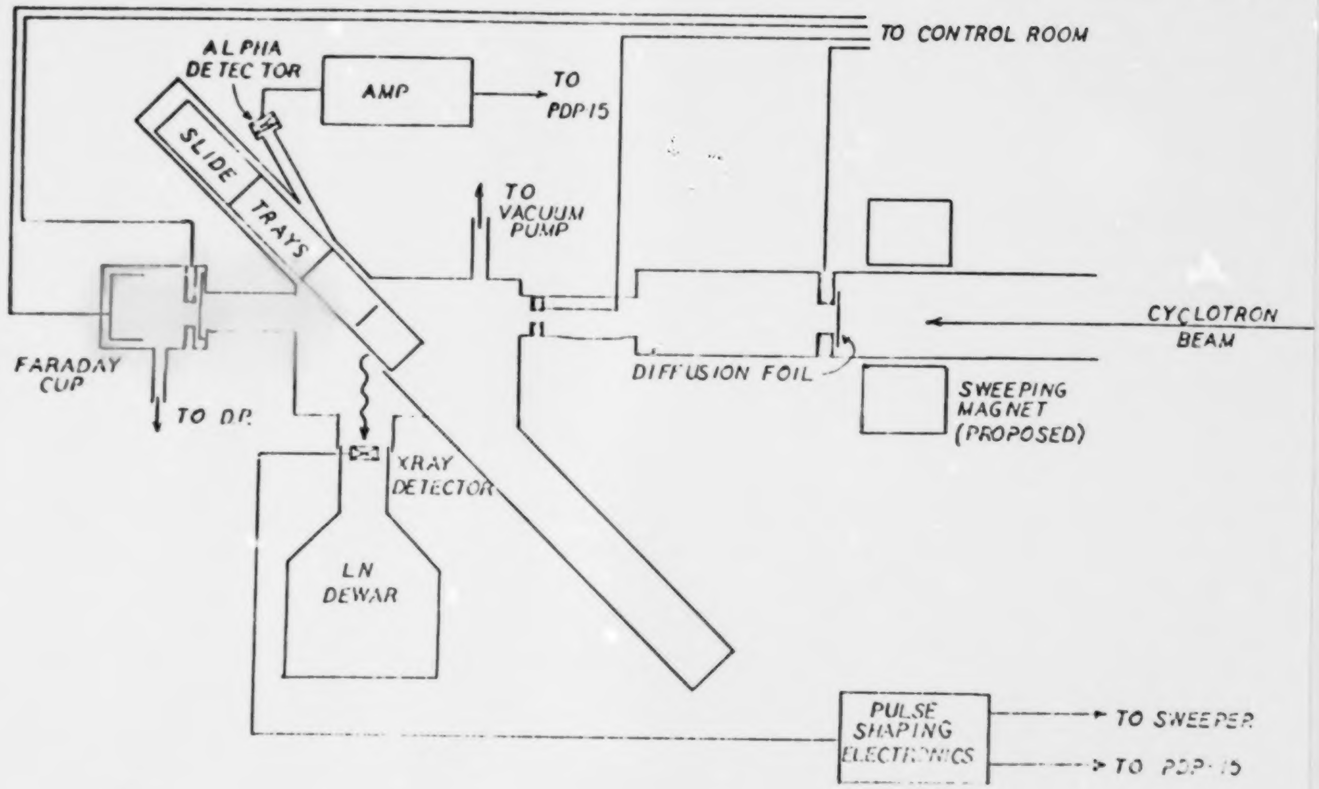
TO CONTROL ROOM
ALPHA DETECTOR
AMP
TO PDP15
SLIDE
TRAYS
TO VACUUM PUMP
CYCLOTRON BEAM
FARADAY CUP
TO DP
DIFFUSION FOIL
SWEEPING MAGNET (PROPOSED)
XRAY DETECTOR
LN DEWAR
PULSE SHAPING ELECTRONICS
TO SWEEPER
TO PDP-15

Figure 2.8. UCD elemental analysis system.

standards. Major effort has been expended in design of the electronics and beam handling in order to insure accuracy in the acquisition of the events comprising N_Z.

The most recent formal analytical intercomparison published is from the EPA/DOE Charleston study (Camp et al., 1978) shown in Table 2.3. Extensive analytical intercomparisons were also included as part of the present program, and their results are given in the Quality Assurance Procedures section and Appendix B.

X-Ray Fluorescence (XRF)--

UCD operates a modern energy dispersive x-ray fluorescence system fully compatible with samples used in the PIXE system. The XRF system participated in the Charleston study (Table 2.3). While most of the SFU samples were done by PIXE, periodic re-analysis by XRF for elements calcium and heavier confirmed quoted PIXE values and achieved improved sensitivities for some transition metals. Figure 2.9 shows performance of the UCD PIXE and XRF groups on polymer films developed by the EPA-Research Triangle Park. The mean ratios to quoted values of the PIXE system were 0.985 ± 0.05, while those of the XRF group were 1.00 ± 0.06.

Forward Alpha Scattering Techniques (FAST)--

The need to gain a better knowledge of the very light elements led to the further refinement of the forward alpha scattering techniques which have been used occasionally at UCD since 1970. In this method, samples on teflon filters are exposed to a 30 MeV alpha beam, and the number and energy of the scattered alphas (and protons from hydrogen) give the amount and mass of elements hydrogen through sodium. An example of a spectrum is shown in Figure 2.10. This technique when coupled with PIXE permits a complete elemental characterization of a sample on a single substrate.

Gravimetric Analysis--

All network samples were analyzed gravimetrically for total mass using a Cahn model 25 microbalance. Comparisons between pre- and post-sampling weights gave accurate mass values. A detailed procedure was developed to handle subtle problems due to electrostatic and filter-filter holder interactions (Engelbrecht et al., 1981) as described in the Quality Assurance section.

TABLE 2.3. COMPARISON OF ANALYTICAL TECHNIQUES. RESULTS ARE MEAN AND STANDARD DEVIATION OF RATIO OF EACH GROUP'S RESULTS TO THE REFERENCE RESULTS

Results expressed as the mean value of the ratio of the results obtained by each laboratory to that obtained by R. Glauque, LBL, with the uncertainty representing one standard deviation.

Group	Method	S	CA	Ti	Fe	Cu	Zn	Se	Br	Pb	All Values	All-Worst
UCD	PIXE XRF	1.01 ±0.07	1.41 ±0.26	1.04 ±0.26	1.01 ±0.05	0.90 ±0.05	1.14 ±0.05	0.93 ±0.05	0.91 ±0.05	0.92 ±0.03	1.03 ± 0.16	0.98 ± 0.08
EPA 1	XRF	0.93 ±0.04	0.89 ±0.06	1.14 ±0.13	0.96 ±0.13	1.04 ±0.13	0.95 ±0.06	0.96 ±0.14	0.92 ±0.05	0.93 ±0.05	0.97 ± 0.08	0.95 ± 0.04
LBL	XRF	0.98 ±0.04	1.27 ±0.13	1.33 ±0.19	0.98 ±0.05	1.02 ±0.07	1.10 ±0.06	0.87 ±0.14	1.16 ±0.06	1.00 ±0.06	1.08 ± 0.15	1.05 ± 0.13
FSU	PIXE	0.89 ±0.05	1.06 ±0.16	1.01 ±0.05	0.94 ±0.04	1.33 ±0.04	1.12 ±0.20	0.49 --	0.92 ±0.07	0.84 ±0.05	0.96 ± 0.23	1.01 ± 0.16
EPA 2	Chem. AA	1.06* ±0.10								1.03 ±0.02		
BNL	Chem.	1.04* ±0.13										
WU.	Gamma Rays	0.54** ±0.15										

*Results obtained for sulfate, divided by 3.
**Results withdrawn during meeting.

LBL - Lawrence Berkeley Laboratory
FSU - Florida State University
BNL - Brookhaven National Laboratory
WU - Washington University, St. Louis, MO.

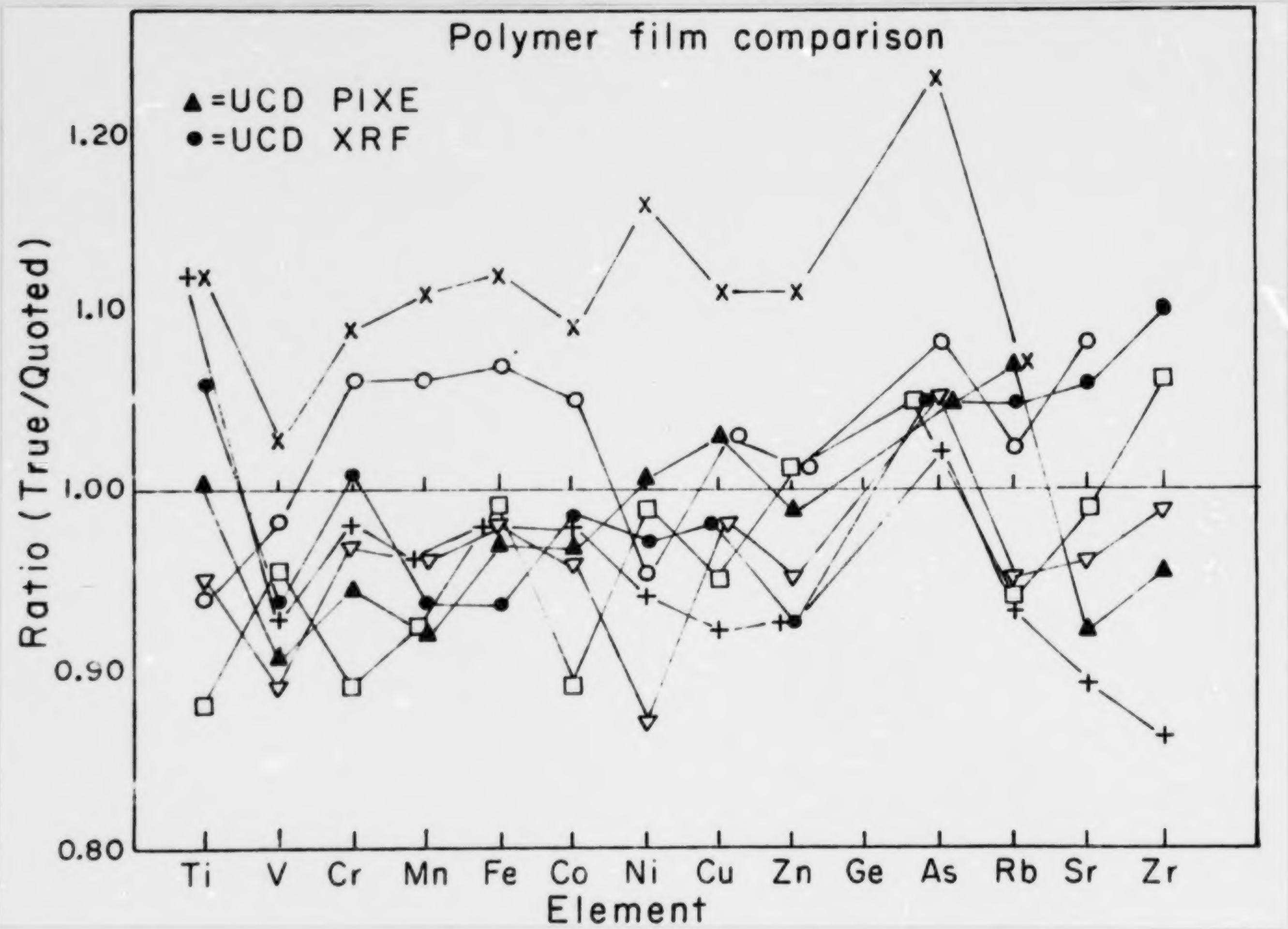

Figure 2.9. Analysis of EPA polymer films.

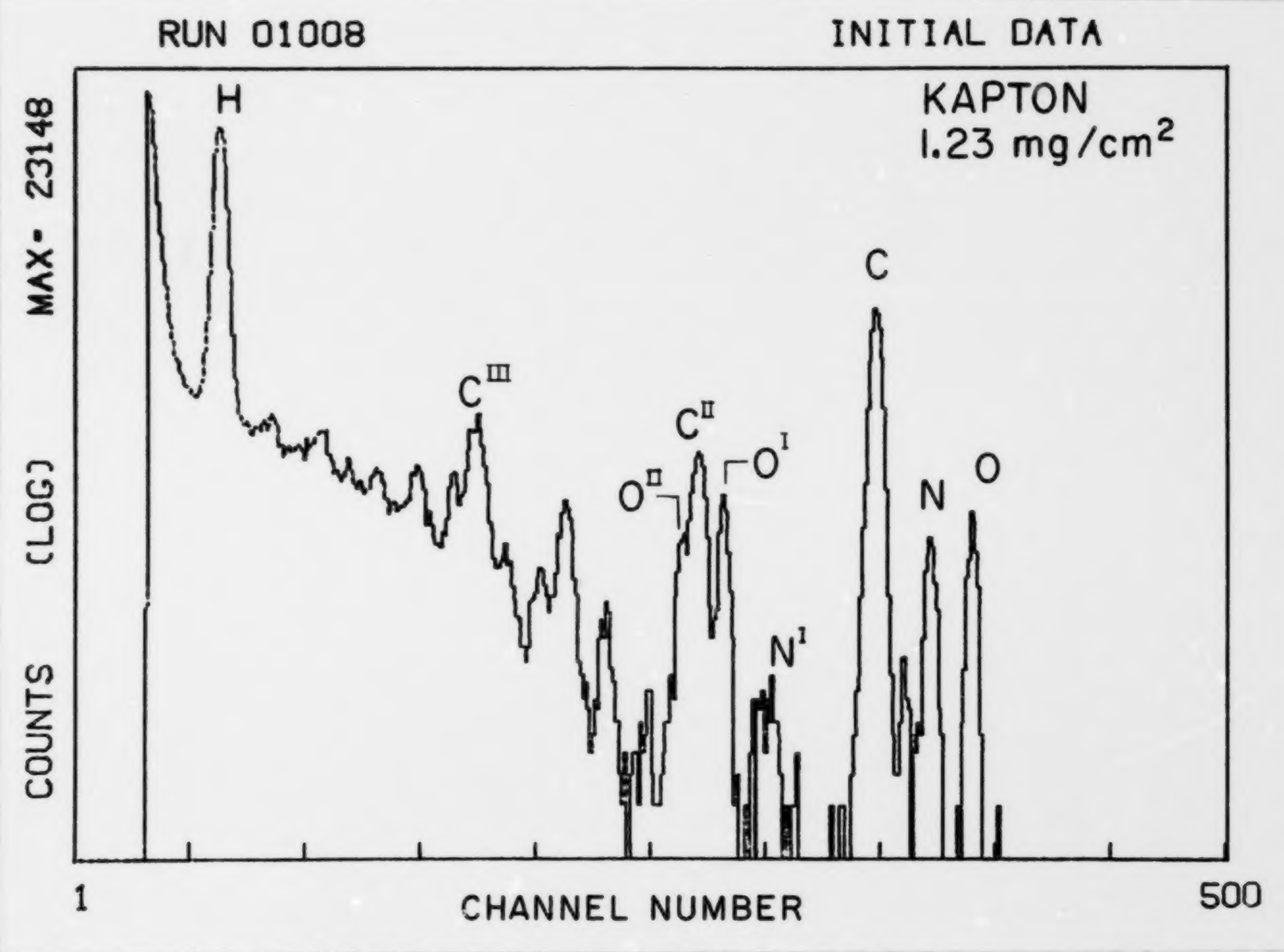

Figure 2.10. Forward alpha spectrum.

Validation of PIXE Analyses

Validation of the analytical system presented a number of problems, since the amount of any given element (Na to U) recorded in an aerosol sample varied from a few nanograms to a few micrograms. The following techniques were used to insure accuracy.

1. In order to determine calibration, 28 gravimetric standards for elements between sodium and uranium were purchased. The values for each standard were quoted in $\mu g/cm^2$ to an uncertainty of ±5% by the manufacturer. These foils were run in the same configuration as the aerosol samples, and provided primary calibration for the system. Total error was about ±7% in operational conditions.

2. In order to check the standards, as well as to provide calibration for elements for which no standard was purchased, atomic cross sections for ion excitation at a number of ion energies were extracted. These were plotted and fit with a polynomial expansion. This fit resulted in values superior to those provided by individual foils, as shown in Figure 2.11.

3. Calibration of the PIXE system was verified through reanalysis of selected samples by an independently calibrated XRF (x-ray flourescence) analysis system. The XRF system, also located at UCD, was used for studies of losses of volatiles, since no vacuum was required for the x-ray system.

4. Important procedures in the verification of analytical systems are interlaboratory comparisons. Formal and informal interlaboratory comparisons involving UCD PIXE and XRF systems have been conducted regularly since 1973. During 1981 an interlaboratory evaluation of thin polymer films provided data directly relating the use of x-ray emission analysis for determining elemental composition of aerosol particles collected on membrane filters (Dzubay et al., 1981). The data from this study are presented in Figure 2.9. These comparisons confirmed that the quoted standard error of ±10% reported for PIXE analyses was a conservative estimate of system accuracy.

5. Considerable effort was expended at the beginning of every analytical run to verify system operation analysis of six to eight gravimetric standards. In addition, a program of regular reanalysis of aerosol samples was instituted that resulted in about 5% of all samples being checked during each year. The analytical precision can be estimated from the ratio of the standard deviation to the mean for samples which were reanalyzed. The precision of the major soil elements (silicon, potassium, calcium, and iron) was 10-12% for all coarse stage samples and for most fine stage samples. For samples with low soil loadings the precision dropped to 20-25%. The precision for sulfur was 10% for most fine stage samples. For low loadings, the precision for sulfur was around 20%. For moderate loadings of copper and zinc the precision was 15-20%, and 30% for lead. For a given sample the variation of the ratios of elements from run to run was considerably less, with a precision of around 2%.

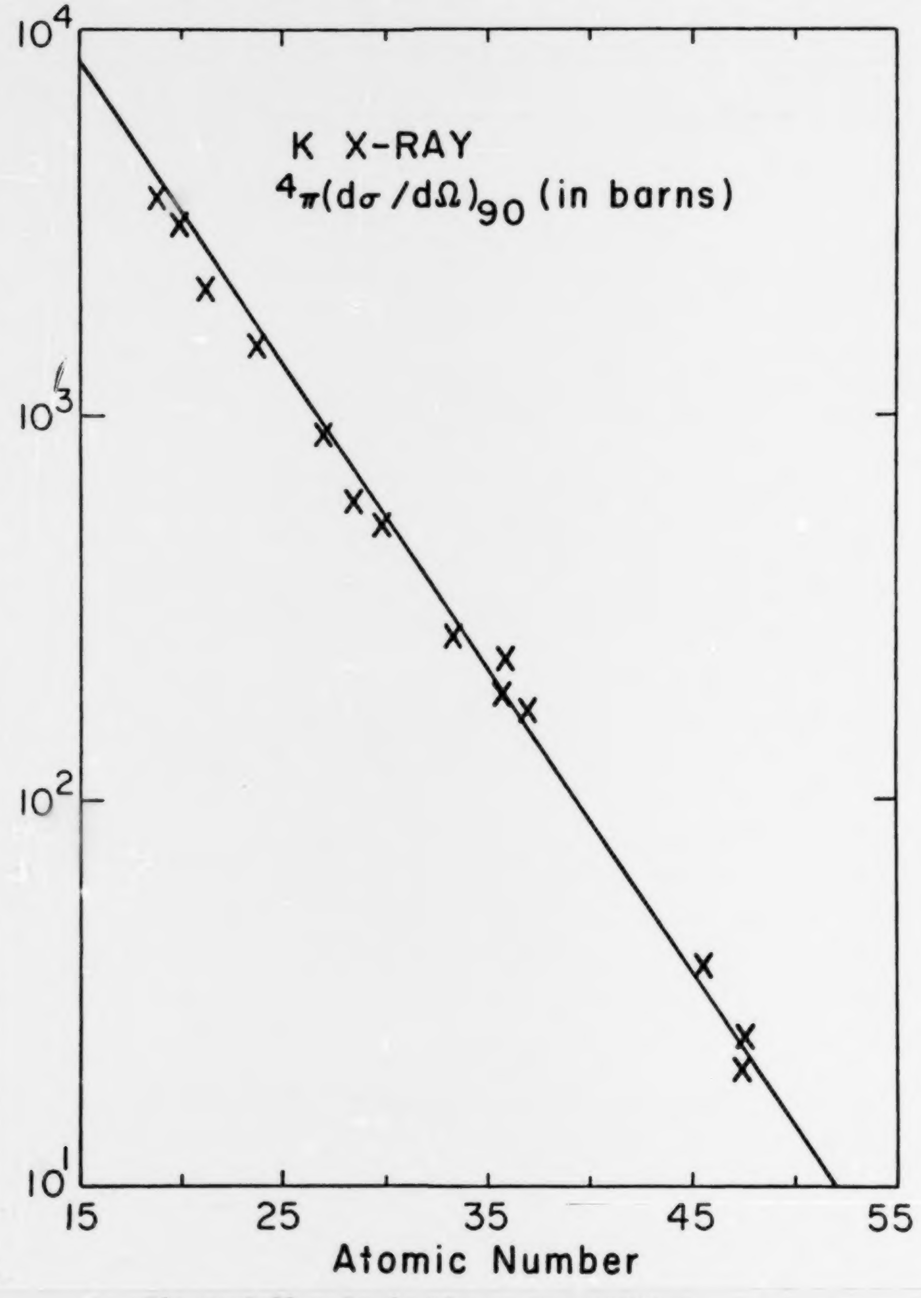

Figure 2.11. Production cross sections.

6. Tests have been made to detect changes that occur in samples during exposure to vacuum and beam irradiations. In samples run to very high excitations (65 times normal integrated beam flux), some loss of halogens has been detected (25%). This effect appeared to be linear with excitation, and thus was negligible for normal analysis. Likewise, in exposure to vacuum for 24 hours, 8 times normal exposure, no loss of any element on a sample was detected ($< 5\%$).

7. Other effects such as beam energy loss through the aerosol samples and filter backing have been calculated. The resulting change in cross section is negligible ($< 5\%$), so no change in calibration is needed versus sample loading. Beam scattering by the sample was also calculated and measured, as it could reduce the beam seen by the Faraday cup. This too was found to be negligible.

X-ray Matrix Corrections

Matrix corrections are necessary to compensate for the absorption of x-rays before reaching the detector. These involve the product of the mass absorption coefficient and the path length through the material. There are two types of corrections: that due to the finite size of the particle from which the x-ray was emitted, and that due to a thin layer of very small particles.

When the material is deposited as separate particles of finite size, the correction is given by an integral over the particle size range of the samples collected. This integral includes the ambient mass distribution for the particle. It is assumed that the particles for each element follow a bimodal mass distribution as found in the California Aerosol Characterization Experiment (Hidy et al., 1975). The relative contribution of each element by particle size was selected on the basis of three years of data collected by UCD for the California Air Resources Board in California urban areas. Each particle is assumed to contain the standard oxide of the elements found, except for NaCl and PbBr. The size dependent collection efficiency for the SFU is incorporated into the size corrections shown in Table 2.4. These values are the inverse of the fraction lost by absorption.

When the material is deposited as a thin layer of small particles, the correction depends only on the thickness and the composition of the material. The thickness is estimated from the sum of all x-ray masses multiplied by 7 to account for low z elements. The composition was estimated from a large number of samples from California that were analyzed for all elements, including H to F. The mass absorption coefficients are similar to those for cellulose. These layer corrections are much smaller than those for size, except for very heavily loaded samples. They are only applied for fine stages. Typical corrections for average and 10 times average mass loadings 10 $\mu g/cm^2$ and 100 $\mu g/cm^2$ are given in Table 2.4.

TABLE 2.4. SELF-ABSORPTION CORRECTIONS FOR PIXE ANALYSIS

	Size Correction		Layer Correction	
Elements	Coarse	Fine	10 μg/cm^2	100 μg/cm^2
Na	2.16	1.08	1.02	1.21
Mg	2.12	1.30	1.01	1.12
Al	1.83	1.22	1.01	1.08
Si	1.45	1.12	1.01	1.05
P	1.33	1.03	1.00	1.04
S	1.16	1.01	1.00	1.03
Cl	1.25	1.02	1.00	1.03
K	1.10	1.03	1.00	1.02
Ca	1.10	1.03	1.00	1.01
Ti	1.07	1.02	1.00	1.01
V	1.05	1.00	1.00	1.01
Cr	1.06	1.00	1.00	1.00
Mn	1.05	1.00	1.00	1.00
Fe	1.05	1.01	1.00	1.00
Ni	1.04	1.00	1.00	1.00
Cu	1.04	1.00	1.00	1.00
Zn	1.04	1.00	1.00	1.00
Br	1.04	1.00	1.00	1.00
Pb	1.06	1.00	1.00	1.00

Minimum Sensitivities

The minimum detection limit for each element is calculated from the background in the x-ray spectrum at the energy of the primary peak. Table 2.5 lists the detection limits assuming that the minimum number of counts in the peak equals 3.29 times the square root of the background counts under the peak. The table gives the average minimum sensitivities for standard 3-day samples, including matrix corrections. The limits for lightly loaded samples are slightly lower than these average values, since the beam current is increased and there is no background from the loading. The sensitivities changed significantly on three occasions. First, a new detector system with improved resolution, installed in early 1981, was used to analyze fine-stage filters collected after November 1, 1980, and coarse-stage filters after January 1, 1981. Second, the analysis time for the coarse-stage filters was decreased for samples collected after April 1, 1981, in order to reduce analysis costs. Third, the SFU samplers were modified in June 1982 to use 25 mm teflon fine-stage filters with active areas of 27% of those used previously. (The field tests for this modification were performed at selected sites during the summer of 1981.) Since the backgrounds produced by the two substrates are similar, the minimum sensitivities were decreased by a factor of 4. Though not applicable for the data covered by this report, the average minimum sensitivity values for samples taken between June and November 1982 are included for comparison.

In the data set provided on magnetic tapes, the minimum sensitivities are based on a more conservative definition of minimum detection limits, with values approximately twice those in Table 2.5 for Na through Zn and 5 times those for Se, Br, and Pb. No measured values were eliminated because they were below the calculated limit. When an element was not found, the negative of the minimum detection limit was stored instead of a measured concentration.

Table 2.5 also includes the percentage of time that each element was detected. Fine S and coarse and fine major soil-derived elements were found on almost all samples. The ambient concentrations of most other elements were near the minimum sensitivities for samples through 1981 and were found on less than 1/3 of the samples. With the more sensitive fine stages of 1982, several important elements were also found on a majority of the samples: Cu, Zn, Pb, Na, and Ti.

Validation of Gravimetric Analyses

Weighing of the Nuclepore filters was performed on a Cahn 25 electrobalance with a printer. Filters were initially passed over a ^{210}Po source to remove any static charge. The filters were then stored between aluminum sheets for three weeks to allow any remaining charge to leak off. Each filter was then passed over the ^{210}Po source again, then it was preweighed, mounted in a filter holder and sent to a site. Upon returning, the filters were removed from the filter holders, checked for damage, passed over the ^{210}Po source, postweighed, and stored for PIXE analysis. These procedures were checked with calibration weights and regular reweighings of control filters. The balance was calibrated 1 to 3 times a day.

TABLE 2.5. ELEMENTAL ANALYSIS MINIMUM SENSITIVITIES AND FRACTION OF TIME FOUND

	Minimum Sensitivities (ng/m^3)						Percentage Found		
	Coarse			Fine			Coarse	Fine	
	7/79 to 12/80	1/81 to 3/81	4/81 to 10/81	7/79 to 10/80	11/80 to 10/81	6/82 to 11/82	7/79 to 10/81	7/79 to 10/81	6/82 to 11/82
Na	70	37	90	28	18	5.2	11	36	62
Mg	43	23	61	20	15	4.7	15	21	46
Al	35	19	50	19	13	3.2	67	56	85
Si	27	16	39	15	12	2.8	97	93	99
P	22	14	33	13	10	2.5	5	9	8
S	17	10	27	11	9	2.1	43	98	100
Cl	16	10	26	11	8	2.0	15	6	1
K	10	7	19	7	6	1.8	97	92	100
Ca	7	5	14	5	4	1.4	99	92	92
Ti	6	4	11	4	4	1.2	67	24	60
V	6	4	11	5	4	1.2	10	6	7
Cr	6	4	10	4	4	1.2	7	12	8
Mn	5	4	9	4	3	1.1	35	11	38
Fe	5	3	8	4	3	1.0	99	91	100
Ni	4	3	6	3	2	0.9	5	5	14
Cu	4	2	6	3	2	0.8	14	13	54
Zn	4	3	7	3	2	0.7	11	21	82
Se	4	2	7	3	2	0.7	3	2	--
Br	5	2	9	4	2	0.7	16	8	40
Pb	10	4	18	8	4	1.5	11	27	67

There were 950 reweights for preweighing and 950 reweights for postweighings throughout the study. Filters were reweighed by a different operator on the same day as the initial weighing. The average difference was 0.0 ± 6.0 μg/filter (equivalent to 0.0 ± 0.14 μg/m^3) for the preweights and 0.0 ± 5.8 μg/filter (0.0 ± 0.13 μg/m^3) on the postweights.

Five hundred control filter cartridges were kept over the 26-month project. Each control cartridge was loaded in the same way as the field cartridges and kept at UCD for an average of 6 weeks before postweighing. The average weight change was 38.65 ± 6.7 μg/filter (0.89 ± 0.16 μg/m^3) for the fine filters and 3.7 ± 11.1 μg/filter (0.09 ± 0.26 μg/m^3) for the coarse filters. Approximately 100 filter cartridges were returned to Davis unused. The average weight gain was 43.7 μg/filter (1.01 μg/m^3) for the fine stage and 24.1 μg/filter (0.56 μg/m^3) for the coarse stage. All fine gravimetric values were corrected for a weight gain of 40 μg (0.92 μg/m^3).

QUALITY ASSURANCE PROCEDURES

All aspects of the program have been subject to extensive quality assurance procedures in order to establish both the accuracy and uncertainties of the data. Detailed procedures for quality assurance are documented in the project's Quality Assurance Manual. A summary of these procedures can be found in Appendix C, while the major findings are given here. The quality assurance procedures fall into two catagories: the internal procedures developed, used, and published by the UCD since 1972, and procedures used by an external quality assurance auditing group designed and implemented for the present program by the Rockwell International Environmental Monitoring and Services Center for the EPA. The UCD quality assurance coordinator for this program, Lowell L. Ashbaugh, was responsible for maintaining, implementing, and updating quality assurance procedures and coordinating with the external audit group.

Internal Quality Assurance

All internal quality assurance activities were documented in the 135-page UCD Quality Assurance Manual that governed all aspects of the program. The internal quality assurance procedures were designed to provide verifications of accuracy and precision of results independent from the methods described earlier for analysis validation. In the case of gravimetric analysis results, this involved parallel handling of loaded filter cassettes sent to fixed sites and returned without being exposed to an air flow. In some cases, such samples arose accidently (e.g., from pump failure). One hundred filter cartridges were available as "field" blanks. Pre- and post-gravimetric analysis of field blanks indicated a weight gain for fine filters equivalent to 1.0 μg/m^3. This compared well with the weight gain value of 0.89 ± 0.16 μg/m^3 measured using the 500 control filters maintained at UCD. The reason for this gain (isolated only during the last year of the program), was transfer of material from the O-ring in the Nuclepore cassette to the filter. Good agreement between laboratory measurements, field blank results, and mass estimates made from the PIXE data supported the correction of the fine-stage gravimetric results by 0.92 μg/m^3. The coarse-stage gravimtetric values, however, differed between laboratory control values, 0.09 ± 0.26 μg/m^3, and field blank values, 0.56 μg/m^3. Reasons for this discrepancy are being examined through study of external contaminations, filter nonuniformity, and other aspects, but this difference has prevented any corrections for coarse mass gravimetric data.

Internal quality assurance procedures for PIXE and XRF data were handled by a program of reanalysis. Typically, PIXE analysis is conducted in one multi-day run per month. During each such run, selected samples from each analysis run during the past 12 months are reanalyzed. Originally, samples were selected randomly, but better coverage is achieved if samples are chosen to represent both extreme and average loading conditions and different sites in the network. Agreement between the values generated in each analysis of these samples guarantees that no drift in calibration has occurred in the past year for typical samples. These data also provide evidence on the ability of samples to stand repeat exposure to vacuum and radiation without detectable changes in various elemental species (i.e., sulfur, halogens, etc.). During the entire period of this work, mean accuracy from the reanalysis procedure agreed very well with the calibration standards, confirming absolute accuracies to ± 5%.

External Quality Assurance

External quality assurance audits were handled by Rockwell International for this program. The areas covered by this program included audits of gravimetric and elemental analysis of particle samples and sample flow rates, and an overall systems audit which reviewed and critiqued all pertinent procedures and systems. Weight audits using NBS traceable, Class M weights, showed that absolute mass determinations were in agreement to a few micrograms. More relevant to the determination of sample mass by the difference of pre- and postweights is the weight differences for the audit weights which were often accurate to better than 1 microgram, equivalent to an uncertainty of ± 0.03 $\mu g/m^3$ for this program. Flow audits were designed to check operation of field units, and they proved very useful in helping UCD track down problems in the flow regulating systems. Two major flow audits gave mean differences of -0.9% and -1.2% between unit readings and calibration devices, but a scatter of 14% occurred between units. The problem in regulator drift was traced to the erosion of a teflon seal and was corrected late in the program. Field audits at the sites confirmed proper operation of the unit, maintenance, and operator training. Analytical audits confirmed that the "UCD PIXE Technique is fundamentally sound and is capable of measuring elemental concentration on a filter." Details are found in Appendix C.

In summary, the quality assurance procedures used in this study were more detailed and formal than any others known to the investigators. They were a major factor in our confidence in these data and the success of the program.

CHAPTER 3

STATISTICAL SUMMARIES OF DATA

GENERAL CONSIDERATIONS

This statistical summary is based on the SFU measurements from July 1979 through September 1981, excluding samples which had heavy fallout from the eruption of Mt. St. Helens on May 18, 1980. Statistics involving gravimetric mass are from October 1979 through September 1981.

The concentrations of the various elements for both coarse and fine particles followed the usual lognormal distribution. Figure 3.1 shows a set of probability distributions for a typical site. The cumulative frequency of the number of cases falling below a given concentration are plotted versus the log of the concentration. The axes are arranged so that a lognormal distribution will follow a straight line, while a normal distribution will curve upward. Since these data are more closely represented by a lognormal distribution, then a normal distribution, the median concentration is best characterized by the geometrical mean, rather than by the arithmetic mean.

COARSE PARTICLES

The geometric mean concentrations of the major elements on the coarse stage are given in Table 3.1. When the concentration of an element was below the detection limit of the PIXE analysis system, a value of 1/2 of the minimum sensitivity was used in calculating the mean. The table should be used in conjunction with Table 3.2 which shows the fraction of time that each element was detected. This fraction depends on the analytical minimum sensitivity and the ambient concentration. When the fraction was significantly below 50%, then the average concentration was dominated by the minimum sensitivities, and does not reflect the average ambient concentration.

The two tables both show that the coarse particles were dominated by six soil-derived elements, Si, Al, Ca, Fe, K and Ti. The coarse concentrations of the major soil elements were highly intercorrelated, with bivariate correlation cofficients at a given site generally exceeding 0.90. Figure 3.2 shows the correlation of iron with coarse gravimetric mass and three of the soil elements for a typical site. The small intercept for the plot of iron and gravimetric mass shows that there was no systematic offset in either analytic technique, while the good correlation indicate no problems with analytical nonlinearity.

The high intercorrelation between the soil-derived elements makes it reasonable to define a soil parameter as the sum of the concentrations of the soil individual elements plus the related concentration of oxygen, if the elements are assumed to be in their standard oxide forms: SiO_2, Al_2O_3, CaO,

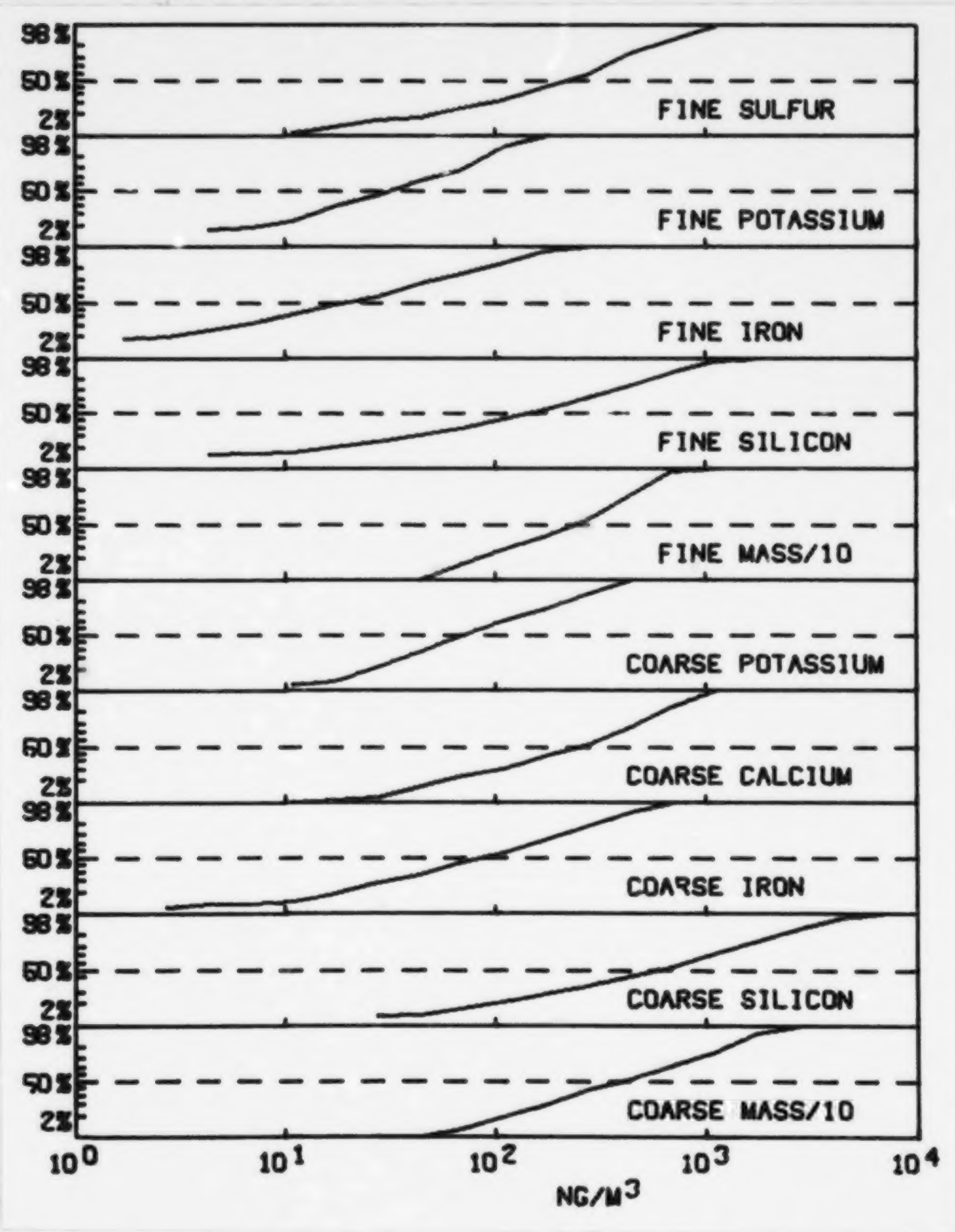

Figure 3.1. Probability plot (lognormal) Carlsbad Cavern 7/79 - 9/81.

TABLE 3.1. COARSE-STAGE GEOMETRIC MEAN CONCENTRATIONS 7/79 - 9/81

Nanograms/M**3

Site	S	Al	Si	Ca	Fe	Cl	K	Ti	Mn	Cu	Mass
1	26	76	372	76	63	19	58	10	6	4	2900
2	27	174	1092	166	158	22	108	18	7	5	5800
3	30	150	915	199	147	22	93	16	7	4	5200
4	35	208	1210	315	189	23	121	21	9	5	8200
5	20	69	238	57	47	35	41	10	6	4	2400
6	32	458	2246	703	710	22	220	34	18	5	15500
7	30	168	934	196	185	22	100	17	8	5	5700
8	29	114	1040	303	143	23	95	16	16	5	7400
9	23	69	215	42	32	22	37	10	6	4	1900
10	38	119	615	322	100	21	74	13	7	5	4200
11	24	179	1027	183	164	20	127	20	8	4	6300
12	27	130	1019	196	152	21	100	17	10	4	5900
13	20	57	185	46	31	19	33	9	6	4	1600
14	23	141	769	614	131	19	79	11	6	4	5800
15	24	85	410	237	71	21	60	10	6	4	3200
16	33	196	1478	550	294	21	144	18	37	5	10300
17	24	190	954	421	152	21	109	16	7	5	5700
18	27	171	910	355	166	20	105	15	7	4	6300
19	24	114	609	225	162	18	62	11	6	4	3900
20	25	78	382	140	60	21	61	11	6	4	3200
21	31	80	343	313	55	44	54	10		5	3400
22	23	100	472	162	74	21	69	11	7	4	3100
23	21	93	355	75	68	18	57	11	6	4	2300
24	23	90	470	190	76	16	56	10	5	3	3600
25	34	253	1152	441	190	17	121	19	6	4	6900
26	25	179	793	250	153	20	91	15	6	4	5500
27	23	92	345	191	70	22	52	12	6	4	2800
28	24	96	441	165	72	25	92	11	6	4	3400
29	20	141	648	143	124	16	93	17	7	4	4300
30	24	88	308	119	64	26	48	11	7	5	2300
31	23	193	746	143	115	18	68	17	6	4	4000
32	21	103	429	121	72	19	58	11	6	4	2900
33	31	193	901	661	196	25	106	16	7	5	7000
34	25	114	495	189	92	20	60	12	6	4	3100
35	26	122	540	222	91	20	71	12	6	4	4400
36	38	313	1435	434	256	28	185	23	8	7	8600
37	34	206	831	231	177	25	121	18	7	9	5500
38	29	84	348	105	83	19	60	13	6	6	2900
39	35	136	702	308	109	20	101	13	5	4	5100
40	37	204	922	338	169	23	125	15	6	9	6400
All	27	146	732	253	137	23	88	15	8	5	5000

TABLE 3.2. COARSE-STAGE PERCENTAGE FOUND BY PIXE ANALYSIS 7/79 - 9/81

Site	S	Si	Fe	K	Ca	Ti	Al	Mn	Cl	P	Cu	Zn	Pb	Br	Ni	V	Cr
1	43	95	98	95	97	54	52	29	11	7	7	10	10	13	7	9	9
2	28	99	99	97	99	76	71	34	5	3	7	8	10	11	5	9	6
3	46	100	100	96	99	71	71	39	9	3	10	10	11	10	1	10	5
4	50	99	99	99	100	73	81	48	6	2	7	21	3	7	3	6	5
5	17	93	97	94	95	53	50	23	64	9	8	7	7	11	3	19	11
6	47	100	100	100	100	94	85	86	8	3	9	25	12	13	2	5	2
7	49	99	99	98	99	71	71	44	5	4	11	10	8	15	4	11	6
8	41	98	97	97	99	68	50	74	11	3	4	20	12	11	3	9	3
9	20	86	88	93	92	48	41	22	15	12	12	6	11	18	7	17	14
10	68	100	99	98	100	63	66	26	8	4	11	7	8	13	6	8	7
11	23	98	100	99	98	79	73	48	7	5	5	8	9	16	6	10	5
12	36	99	100	100	99	73	66	66	5	4	9	12	9	12	3	9	4
13	17	89	94	90	90	42	37	18	9	12	7	2	6	13	4	21	13
14	27	100	100	99	100	63	73	35	9	3	9	5	12	17	4	8	5
15	42	98	98	97	99	53	61	25	17	6	10	9	10	17	6	10	9
16	49	100	100	99	100	76	71	96	3	1	7	21	12	17	3	4	3
17	26	97	98	97	99	75	73	34	8	6	10	11	17	22	4	6	7
18	49	99	99	99	100	76	77	33	5	5	8	10	10	17	4	8	6
19	47	100	100	97	100	64	68	30	10	8	14	16	10	16	7	6	7
20	42	96	96	96	98	52	52	28	12	7	8	8	3	14	5	11	8
21	40	93	95	95	98	40	51	16	52	7	8	5	7	14	7	13	11
22	35	95	98	96	97	59	62	30	10	6	11	5	9	15	5	12	3
23	33	99	99	95	97	59	65	22	8	8	13	6	12	14	5	13	10
24	60	99	100	99	99	64	66	31	12	3	7	7	3	16	4	8	5
25	62	100	100	90	100	81	78	33	6	1	7	20	16	25	2	5	6
26	45	99	99	98	100	78	75	30	17	2	24	25	25	22	7	7	7
27	37	95	99	93	100	63	64	22	14	5	10	5	9	16	7	7	17
28	39	96	99	99	98	61	65	23	28	4	9	4	8	20	3	12	9
29	34	100	100	100	100	78	84	42	1	3	1	6	0	5	3	9	9
30	30	96	96	95	96	51	62	22	17	7	12	6	9	16	6	8	7
31	39	98	99	98	99	78	83	30	3	2	14	10	16	17	7	14	5
32	35	95	98	95	98	64	65	26	16	7	10	4	8	17	5	14	6
33	52	99	100	100	100	75	78	28	20	1	18	18	23	19	3	7	6
34	49	98	99	97	99	67	68	25	15	6	18	9	16	18	7	9	9
35	52	100	100	98	100	63	68	26	14	4	15	9	11	15	6	13	6
36	54	100	100	100	100	86	84	40	62	2	31	12	16	20	4	5	1
37	62	98	100	99	100	79	79	37	23	3	54	28	17	17	2	10	6
38	60	97	100	98	99	64	60	27	14	6	43	12	12	16	5	10	7
39	66	95	97	97	99	68	62	30	16	2	18	19	17	22	9	5	7
40	69	100	100	100	100	78	81	31	21	0	62	20	13	15	6	8	2
All	43	97	99	97	99	67	67	35	15	5	14	11	11	16	5	10	7

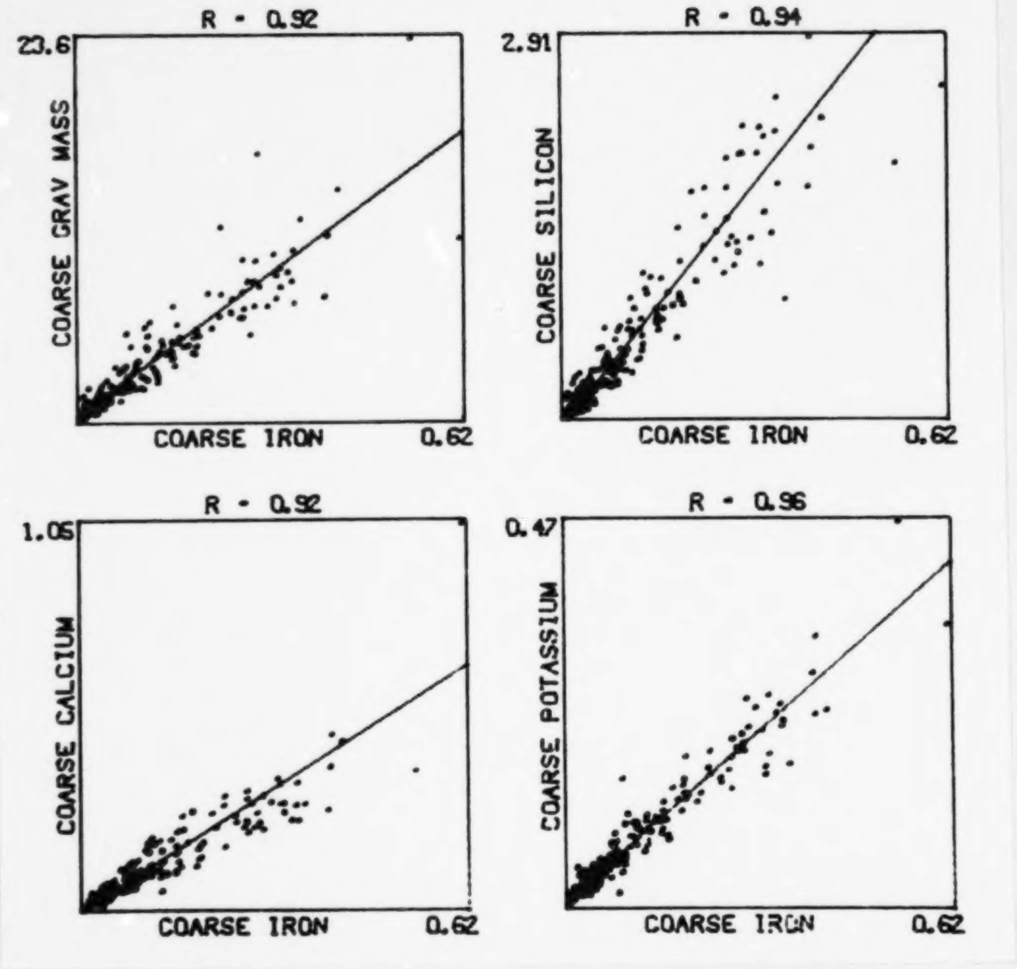

Figure 3.2 Scattergram comparison of coarse elements-Rocky Mountain 10/79-9/81.

Fe_4O_5 ($2FeO + Fe_2O_3$), K_2O and TiO_2. The correlation coefficient between this coarse soil parameter and the coarse gravimetric mass at each site averaged 0.90. However, the coarse soil mass was consistently 1/2 the coarse gravimetric mass. For the 40 sites, the ratio averaged 0.54 with a standard deviation between sites of 0.04.

Figure 3.3 shows the time variation of coarse silicon averaged over various regions of the network. The other coarse elements and the coarse mass follow the same pattern. It is apparent that the coarse soil concentrations were much larger from April to October than they were during the winter months.

The maps in Figures 3.4 to 3.6 show the spatial variation of the coarse soil concentrations for each month of sampling. The diameters of the circles are proportional to the monthly arithmetic mean soil concentrations. The last map shows the average concentrations for the entire period. The most noticeable feature was the sudden increase in soil concentrations in the northwestern Great Plains during April and May.

An additional soil element, manganese, was measured more than 40% of the time at seven sites, all in the northwestern Great Plains. At these sites, manganese correlated strongly with the other soil elements, especially calcium and iron.

Coarse sulfur was found a large portion of the time at one-half of the sites. It correlated with the soil elements at two sites, 21 and 25, both of which are near deserts. Large concentrations of coarse sulfur have also been measured near Owens Dry Lake in California (Barone et al., 1981).

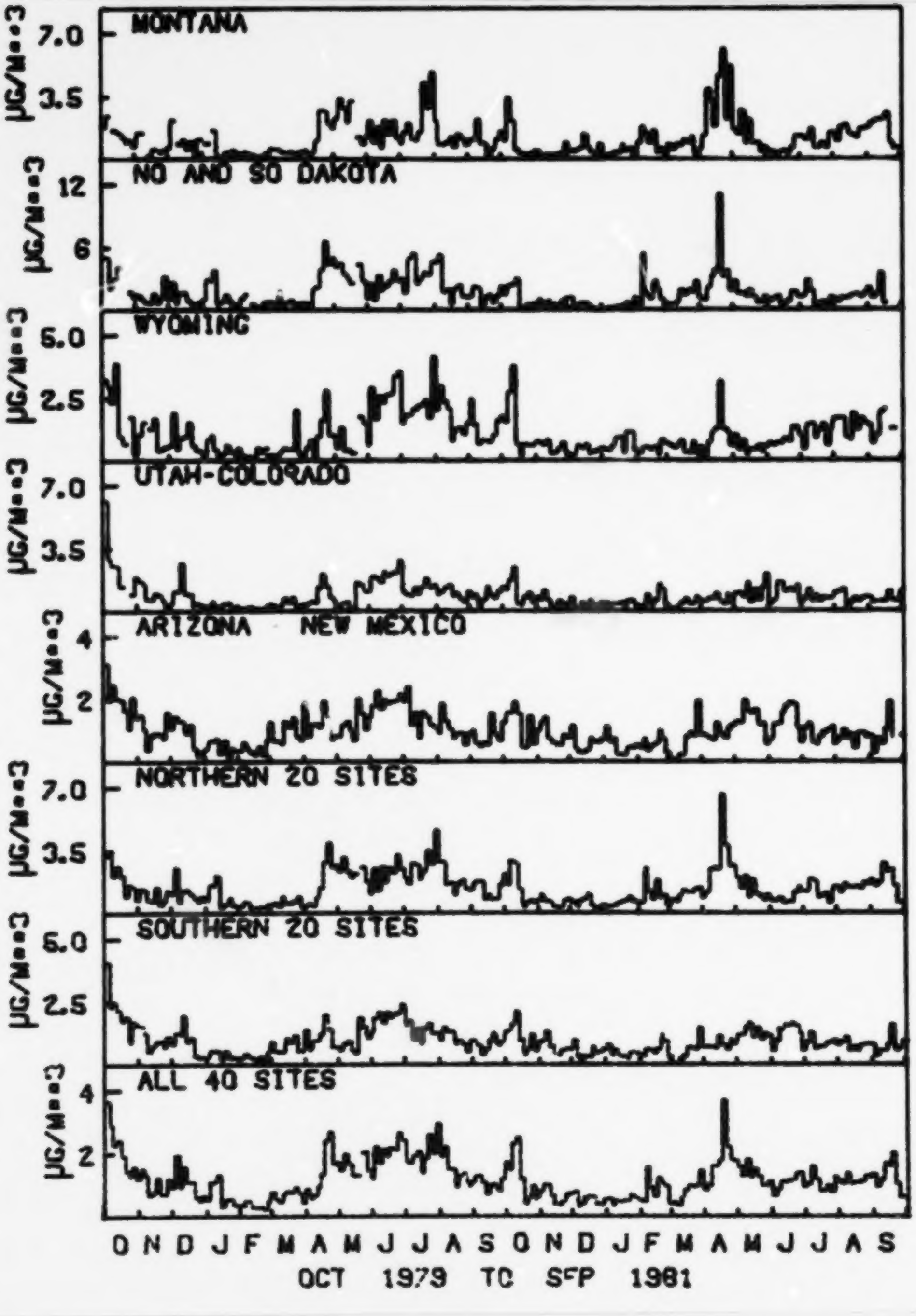

Figure 3.3. Coarse silicon time plot.

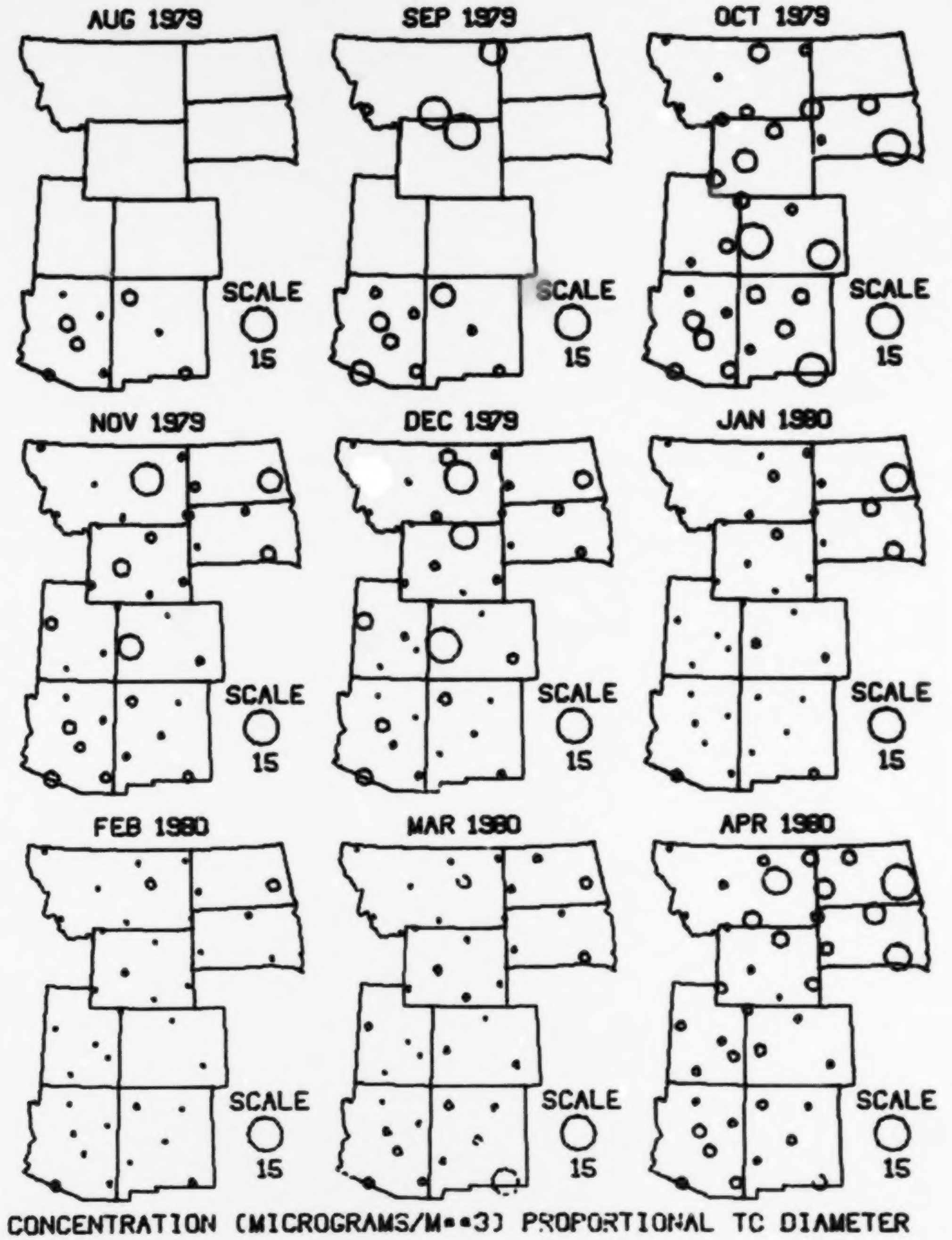
AUG 1979
SEP 1979
OCT 1979
NOV 1979
DEC 1979
JAN 1980
FEB 1980
MAR 1980
APR 1980
SCALE
15
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.4. Coarse soil maps 8/79 - 4/80.

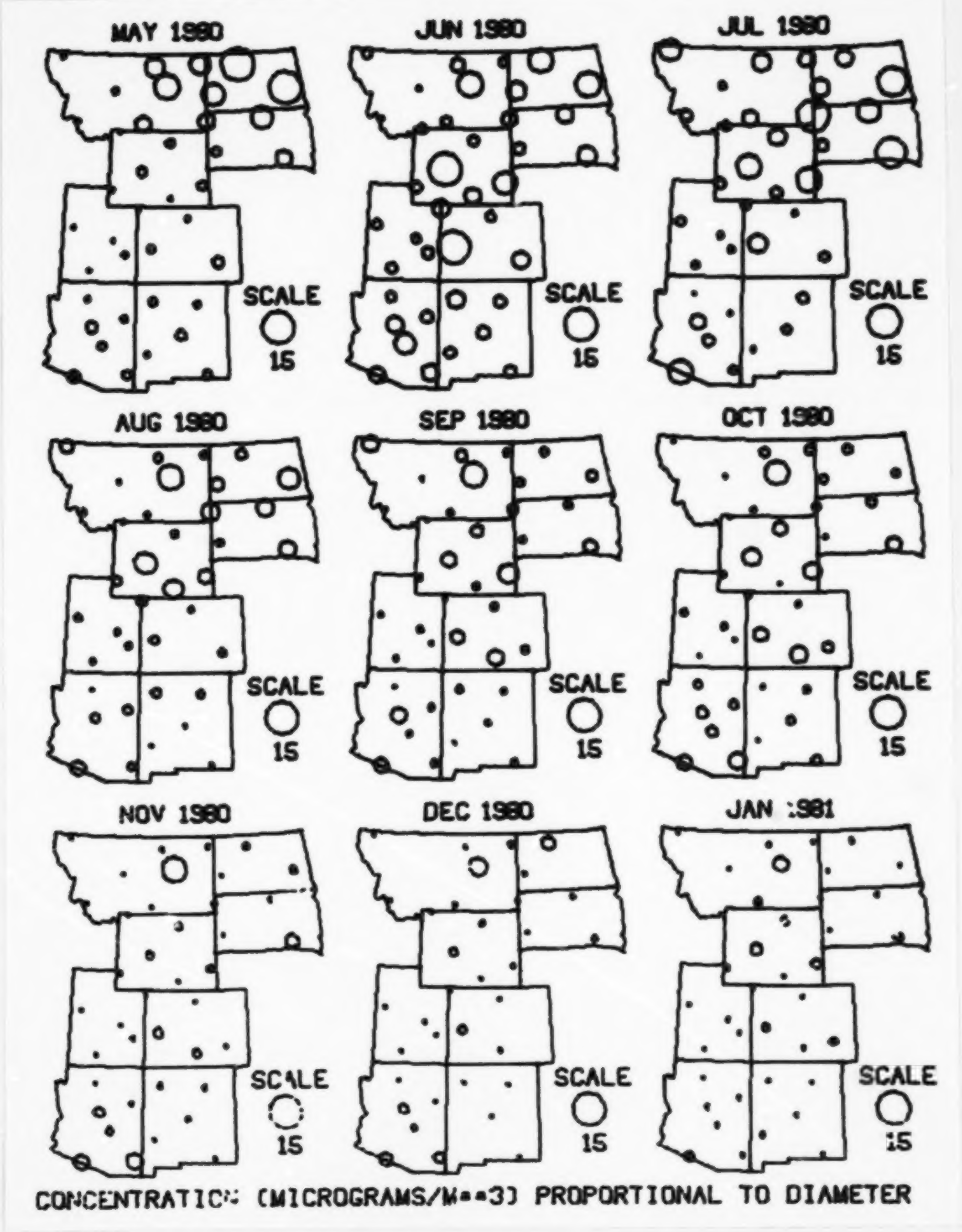
MAY 1980
JUN 1980
JUL 1980
AUG 1980
SEP 1980
OCT 1980
NOV 1980
DEC 1980
JAN 1981
SCALE
15
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.5. Coarse soil maps 5/80 - 1/81.

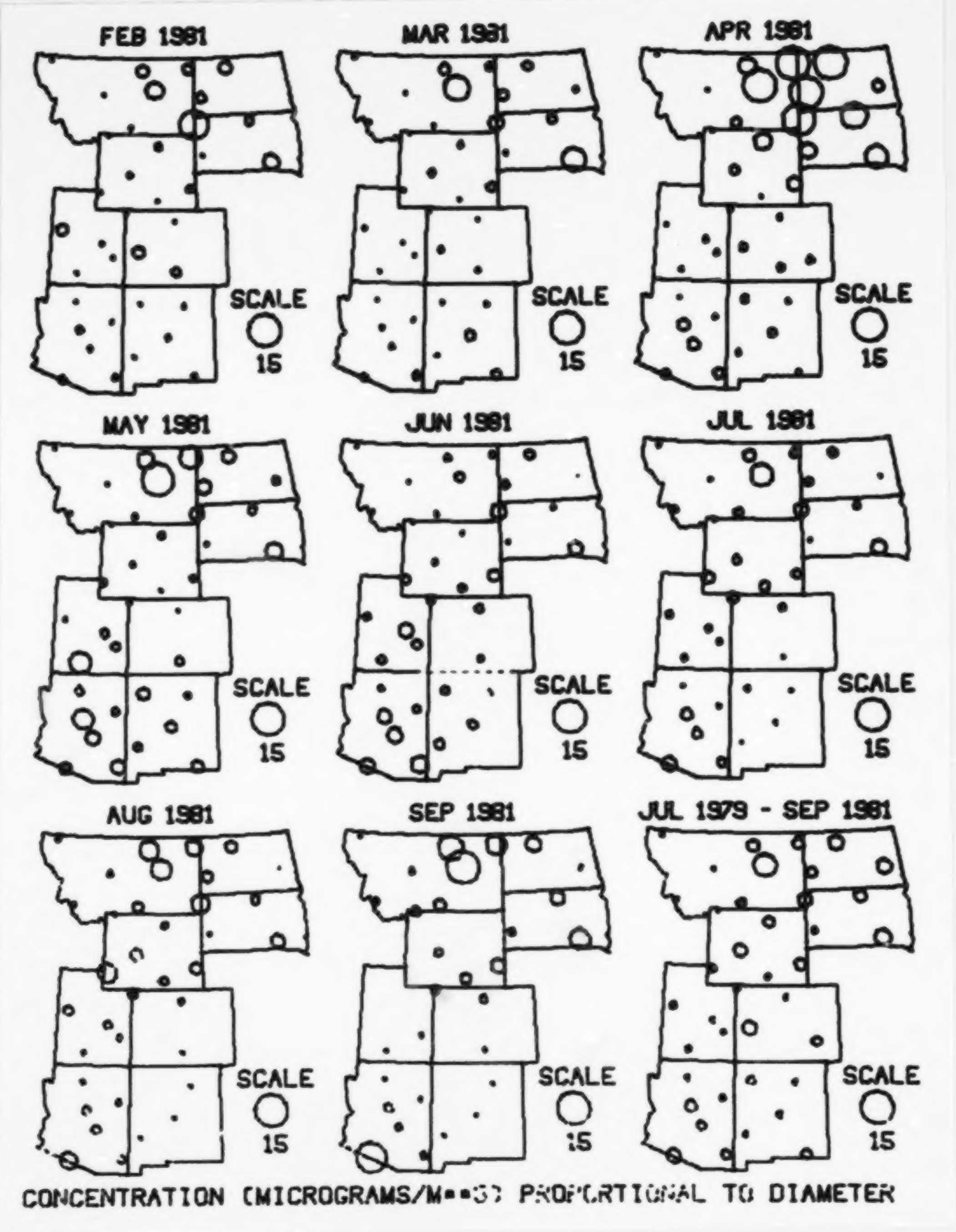
FEB 1981
MAR 1981
APR 1981
MAY 1981
JUN 1981
JUL 1981
AUG 1981
SEP 1981
JUL 1979 - SEP 1981
SCALE
15
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.6. Coarse soil maps 2/81 - 9/81.

FINE PARTICLES

The geometrical mean concentrations of the major elements on the fine stage are given in Table 3.3. When the concentration of an element was below the detection limit of the PIXE analysis system, a value of 1/2 of the minimum sensitivity was used in calculating the mean. Table 3.4 gives the fraction of time that each element was detected. These tables show that of the PIXE measured elements sulfur and soil related elements dominate the fine-stage mass. Samples collected in northern Arizona in the VISTTA study project were analyzed for sulfur via PIXE and for sulfate via ion chromatography. Comparison showed that all of the particulate sulfur was present as sulfate (Macias et al., 1981 a). If the sulfur is assumed to be ammonium sulfate, then the fine sulfate concentration averaged over the network was 1.6 times the fine soil concentration. Figure 3.7 shows the apportionment of the fine gravimetric mass between ammonium sulfate, soil related elements, and smoke for all sites in the network. Ammonium sulfate accounted for 38% of the fine mass, while fine soil contributed 23%. The smoke concentration, as discussed below, is based on the concentration of potassium in excess of that calculated from the soil composition, and on the assumption that potassium in smoke accounts for 5% of the smoke mass.

The correlations between fine gravimetric mass, fine soil and fine sulfur are shown in Figure 3.8, for a typical site. Over the entire network the correlation coefficient between fine mass and fine sulfur averaged 0.66, with typical coefficients between 0.7 and 0.8, but never exceeding 0.8. The correlation between fine gravimetric mass and fine soil was generally lower, with an average value of 0.53. Only at site 11 did the correlation between mass and soil (0.85) significantly exceed that between mass and sulfur (0.35). The correlation between fine mass and the sum of fine sulfate and fine soil was somewhat better than the correlations of each separately, with an average coefficient of 0.78.

Figure 3.9 shows the time variation of fine sulfur, soil, potassium and gravimetric mass for the northern and southern halves of the network. The fine soil tended to follow the coarse soil pattern of higher concentrations in spring and summer. In the north, there were three high-sulfur episodes, in March and May 1980 and August 1981. Generally, the sulfur concentrations were higher in summer than in winter, especially in the south. The smaller increase during the summer of 1980 compared to the summer of 1981 in the south was probably related to the copper smelter strike from July 1980 until October 1980. Fine potassium could be produced by either soil or smoke. Generally it follows the time pattern of fine soil, with the exception of June 1980 and 1981 in the southern states, when the relative concentration of potassium increased. The fine gravimetric mass showed less seasonal variation than did the soil and sulfur.

TABLE 3.3. FINE-STAGE GEOMETRIC MEAN CONCENTRATIONS 7/79 - 9/81

Nanograms/M**3

Site	S	Al	Si	Ca	Fe	K	Ti	Cu	Zn	Pb	Mass
1	215	23	82	16	16	41	4	2	3	11	3800
2	153	37	135	25	23	28	6	3	3	15	2200
3	262	39	137	41	27	34	5	3	3	12	3300
4	225	44	147	57	27	33	6	3	3	13	3300
5	130	26	61	14	11	19	4	2	3	11	1800
6	214	54	213	76	88	38	6	3	3	16	4000
7	273	40	161	35	39	30	6	3	3	12	3300
8	178	29	122	42	21	25	5	3	4	15	2500
9	98	28	77	11	10	17	5	3	3	12	1400
10	220	32	111	59	18	22	5	3	3	12	2100
11	162	40	125	30	23	25	5	3	3	11	2000
12	241	34	128	36	25	27	5	3	3	13	2800
13	86	24	46	11	8	14	4	2	2	10	900
14	169	36	151	81	23	23	5	2	3	11	2300
15	211	30	100	38	17	23	5	2	3	13	2100
16	282	43	199	90	48	38	5	3	4	15	4200
17	158	38	134	52	23	27	5	3	3	20	2700
18	264	40	159	50	33	31	5	3	3	13	3000
19	230	36	120	53	45	22	4	3	3	13	2700
20	140	31	94	28	14	23	5	3	3	11	1600
21	144	31	92	55	15	20	5	3	3	13	1900
22	191	36	100	31	18	23	5	3	3	12	2100
23	189	32	83	19	16	21	5	2	2	12	1800
24	237	35	136	34	22	23	4	2	2	9	2400
25	142	42	167	63	26	33	4	2	3	19	3000
26	214	41	145	48	31	38	5	4	5	16	3000
27	247	39	117	44	23	27	5	3	3	13	2100
28	232	33	97	31	18	33	5	3	3	12	2000
29	187	42	139	32	24	27	5	2	2	8	2100
30	183	34	90	25	16	21	5	3	3	14	1700
31	215	46	174	29	25	23	5	2	3	11	2000
32	204	34	119	26	19	24	5	2	3	11	2000
33	313	49	190	119	42	40	5	3	3	21	3700
34	299	36	126	33	24	24	5	3	3	13	2600
35	305	37	129	40	24	28	5	3	3	12	2700
36	475	66	281	80	49	54	6	4	4	18	4500
37	460	44	175	49	37	41	5	5	8	20	4000
38	357	34	100	26	19	27	5	4	5	13	2400
39	258	44	171	50	26	41	5	3	4	12	2500
40	568	45	202	60	37	41	5	4	6	19	4100
All	233	38	134	43	26	29	5	4	3	13	2600

TABLE 3.4. FINE-STAGE PERCENTAGE FOUND BY PIXE ANALYSIS 7/79 - 9/81

Site	S	Si	Fe	K	Ca	Tl	Al	Mn	Cl	P	Cu	Zn	Pb	Br	Ni	V	Cr
1	99	93	89	97	76	15	46	5	7	10	6	34	18	2	4	7	14
2	97	93	89	91	85	26	53	9	10	11	5	14	20	7	4	6	14
3	100	94	93	96	96	26	54	12	4	8	7	26	15	2	3	6	13
4	98	92	90	94	97	24	64	11	4	10	10	16	14	1	3	4	12
5	97	80	78	87	76	17	43	7	12	14	3	11	9	2	6	5	18
6	99	99	99	97	97	36	72	27	4	6	10	25	43	13	2	4	7
7	99	96	98	95	92	25	56	14	5	11	8	20	17	3	4	3	11
8	99	90	87	89	93	21	43	31	6	8	14	26	32	8	4	9	17
9	93	85	73	75	69	20	33	12	15	19	5	14	19	2	5	8	16
10	100	92	92	89	99	20	48	7	3	9	3	9	15	0	3	6	14
11	97	91	92	88	90	26	56	11	4	9	5	8	9	3	5	9	11
12	99	95	95	93	95	23	49	17	6	5	7	17	20	3	6	7	15
13	96	77	70	77	72	17	40	10	10	18	7	8	9	2	3	9	21
14	97	97	96	89	98	19	58	9	6	6	5	10	18	5	3	4	8
15	100	98	93	92	98	16	50	11	5	10	5	9	25	4	3	8	13
16	98	97	99	97	100	28	61	60	4	7	6	33	30	11	6	3	9
17	98	93	92	93	93	22	58	11	4	9	4	10	49	27	3	8	10
18	99	97	98	96	99	26	64	6	2	10	10	9	30	6	5	6	13
19	99	97	98	87	99	20	57	7	0	22	3	31	30	7	4	4	13
20	95	85	84	87	87	28	46	8	10	15	8	6	11	8	3	7	15
21	99	89	88	87	90	19	40	7	8	13	7	11	17	8	4	4	13
22	98	90	89	88	93	26	56	12	4	14	6	4	15	3	7	4	15
23	98	90	92	89	86	26	52	10	6	10	10	6	27	8	5	5	15
24	99	96	94	93	94	23	62	6	3	5	5	14	22	7	3	5	10
25	100	98	94	98	95	23	66	6	4	7	5	11	46	23	5	3	11
26	99	92	95	93	94	20	57	15	7	4	35	46	44	19	6	7	7
27	99	91	93	91	96	23	56	5	4	7	6	12	19	7	7	7	13
28	98	92	87	90	89	21	51	8	4	6	8	6	19	9	7	6	14
29	99	100	99	98	98	40	77	13	9	11	4	8	5	1	2	3	18
30	98	87	81	82	83	19	48	8	7	10	7	12	24	5	6	9	14
31	98	97	91	88	89	31	64	9	3	6	14	15	24	3	7	6	9
32	97	96	89	90	91	26	59	10	7	13	10	11	16	6	4	7	9
33	100	98	98	97	99	30	69	9	5	7	20	24	62	22	4	5	9
34	100	96	97	94	94	24	60	6	3	6	15	28	31	5	7	4	17
35	100	98	95	97	96	27	61	14	6	9	12	26	23	8	7	5	11
36	99	100	98	99	100	31	73	8	10	3	25	31	39	14	4	4	10
37	100	95	95	96	93	29	60	10	4	5	57	75	61	14	5	3	9
38	98	90	89	94	92	23	57	5	1	12	47	48	27	3	6	4	10
39	97	93	91	92	92	32	51	8	2	7	13	44	28	5	7	9	11
40	100	98	98	98	98	31	67	8	4	2	57	67	60	9	4	5	8
All	98	93	91	92	92	24	56	11	6	9	13	21	27	8	5	6	12

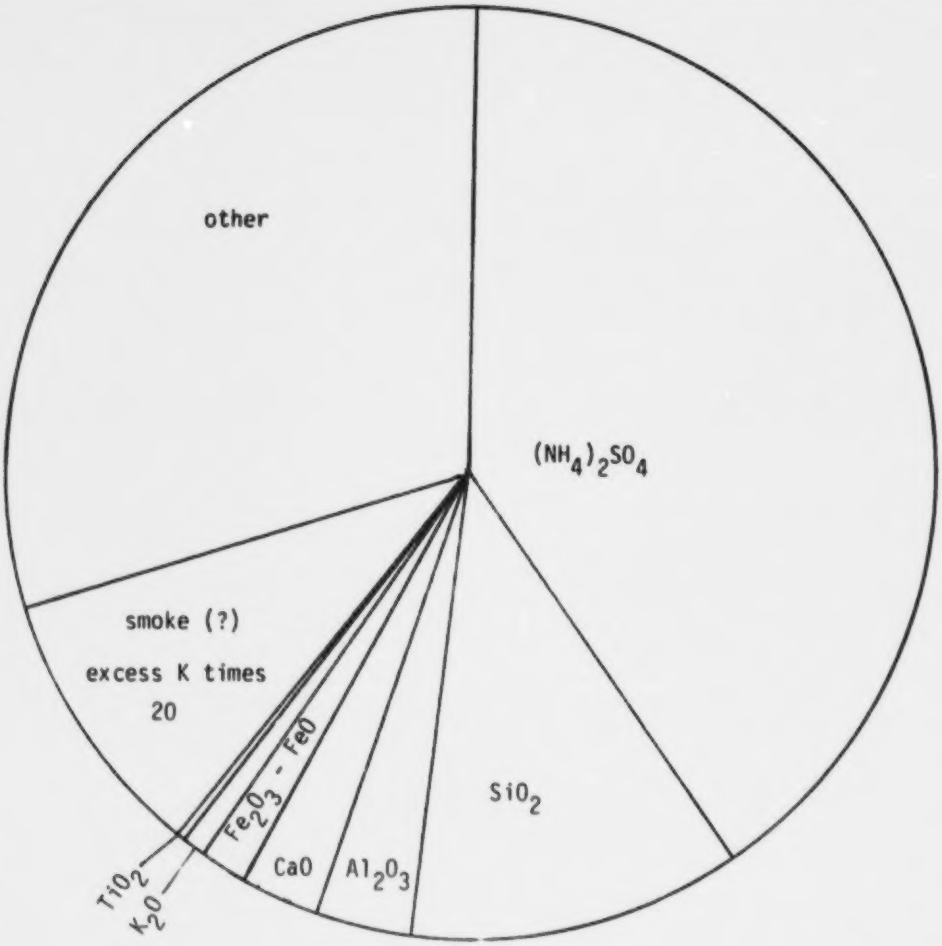

Figure 3.7. Network average composition of fine mass.

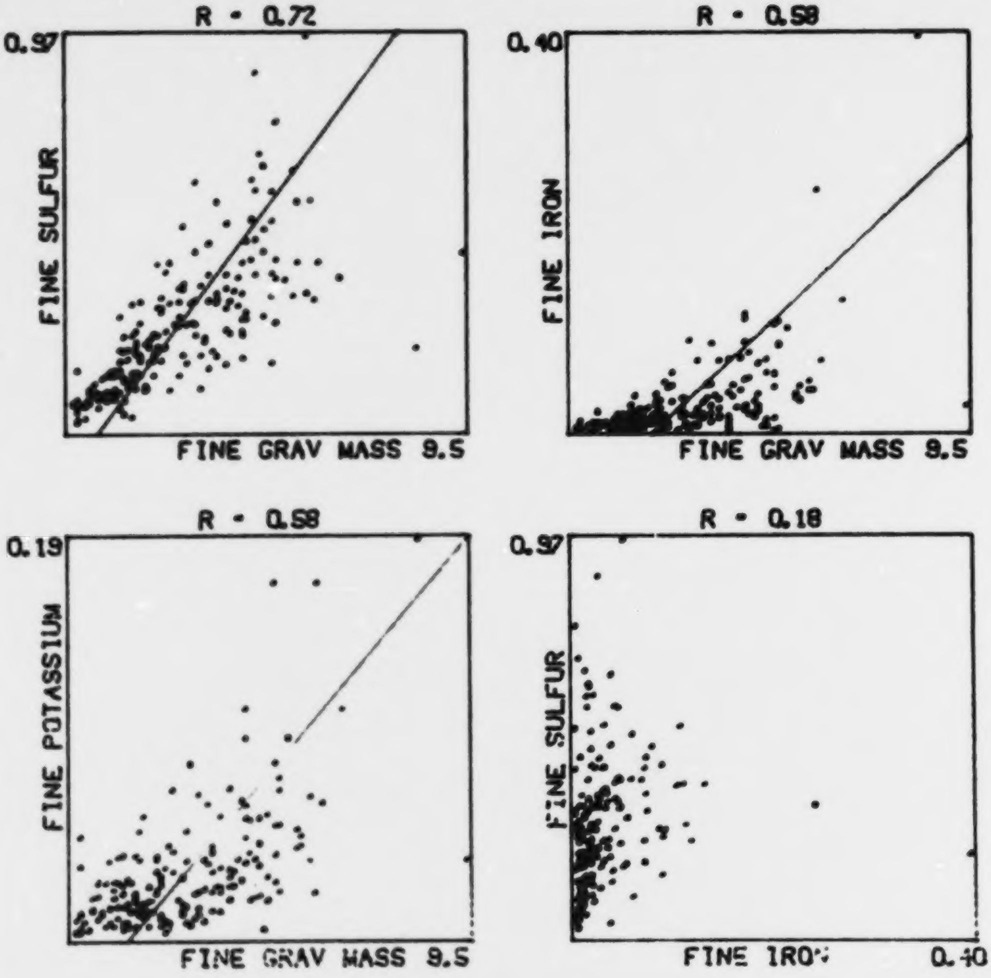

Figure 3.8. Scattergram comparison of fine elements Rocky Mountain 10/79 - 9/81.

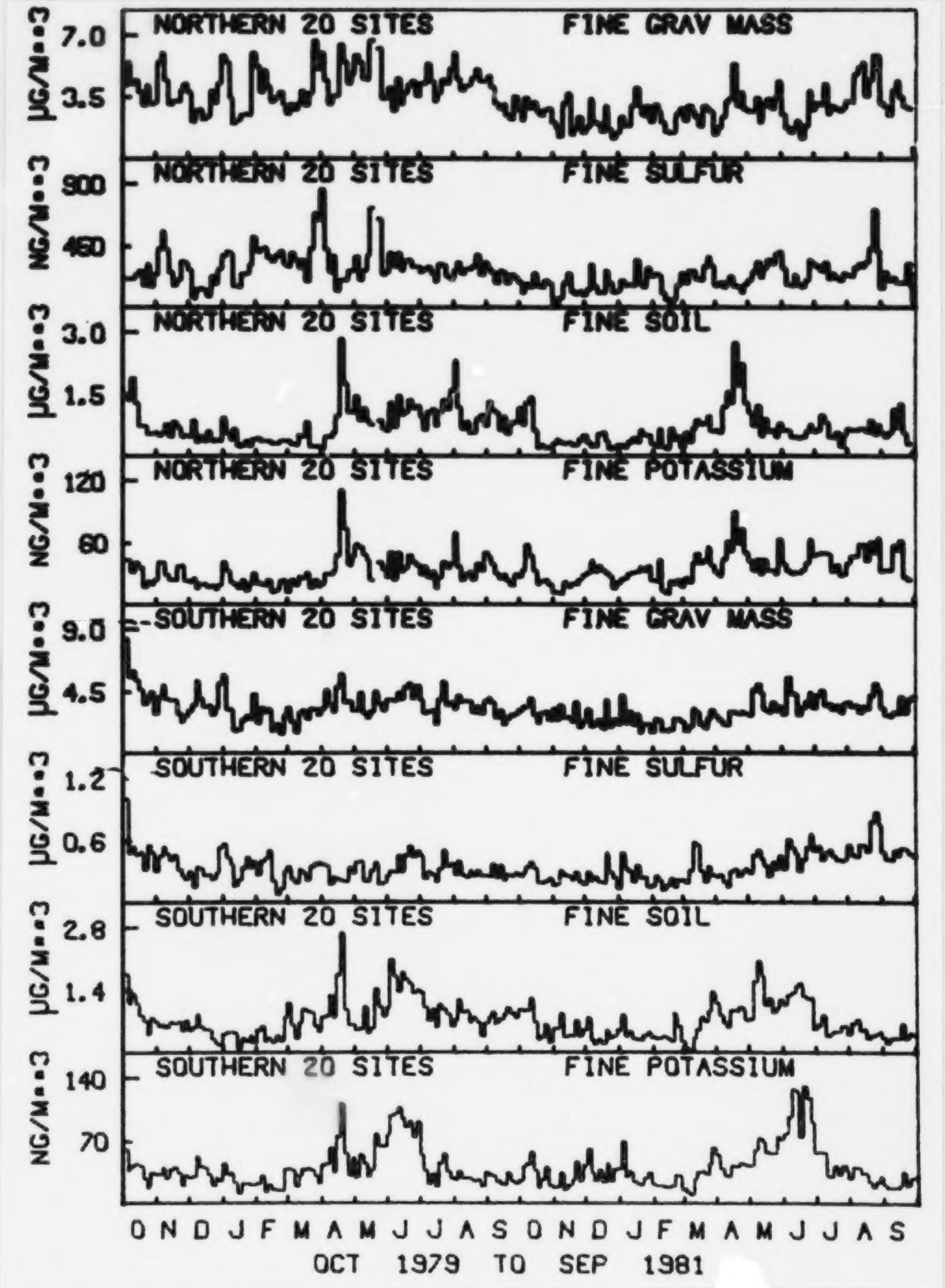

Figure 3.9. Fine particle time plo[illegible]

The maps of Figures 3.10 to 3.15 show the spatial variation of the fine soil and fine sulfur concentrations for each month of sampling. The diameters of the circles are proportional to the monthly arithmetic mean soil concentrations. The last map in each set shows the average concentrations for the entire time period. The fine soil concentrations, like the coarse, increased rapidly in April and May for the northern Great Plains. In Arizona, the fine soil concentrations were greatest in May and June, while fine sulfur was largest from June to October, as long as the smelters were operating. In the northern Great Plains, sulfur was highest during February, March, and May of 1980, and May of 1981.

SIZE DISTRIBUTIONS

Tables 3.5 to 3.7 give the fraction of total mass on the fine stage by site for gravimetric mass, sulfur and iron. Shown are the correlation coefficients between the concentrations in the two size fractions and three estimates of the fine fraction. The first estimate is from the slope of the best-fitting line through the origin in a plot of fine versus coarse. The second estimate is the average ratio of fine to the total, while the third is the ratio of the mean fine to the mean total. A plot of coarse versus fine sulfur at one site is shown in Figure 3.16. The correlations between the coarse and fine concentrations were low for gravimetric mass and sulfur, but somewhat better for iron. The good correlation between the coarse and fine iron indicates that there is probably a common mechanism for producing the iron on both stages. That is, the airborne soil may have a fairly uniform size distribution which overlaps the 2.5 μm separation of the two stages.

Approximately 1/3 of the gravimetric mass below 15 μm was smaller than 2.5 μm. Eighty-eight percent of the sulfur and 18% of the iron were collected on the fine stage.

The size distribution for the less common elements can be estimated from the fraction of times that the element was detected on each stage (Tables 3.2 and 3.4). Manganese, chlorine, and vanadium were predominately on the coarse stage, while lead and zinc were primarily on the fine stage. Copper was equally divided between the coarse and fine stages.

SOIL-DERIVED ELEMENTS

The composition of the soil-related elements in the atmosphere was similar to that of average rocks and sediment, as defined by the CRC Handbook of Chemistry and Physics. Table 3.8 compares the composition relative to iron for the two SFU stages with that for various classifications of rock and sediment. At each site, the ratio was determined by the slope of the best-fitting line through the origin. The table lists the arithmetic mean and standard deviation of the ratios determined for each site. Coarse sulfur is included to show that possibly 1/2 of the coarse sulfur could be soil-derived.

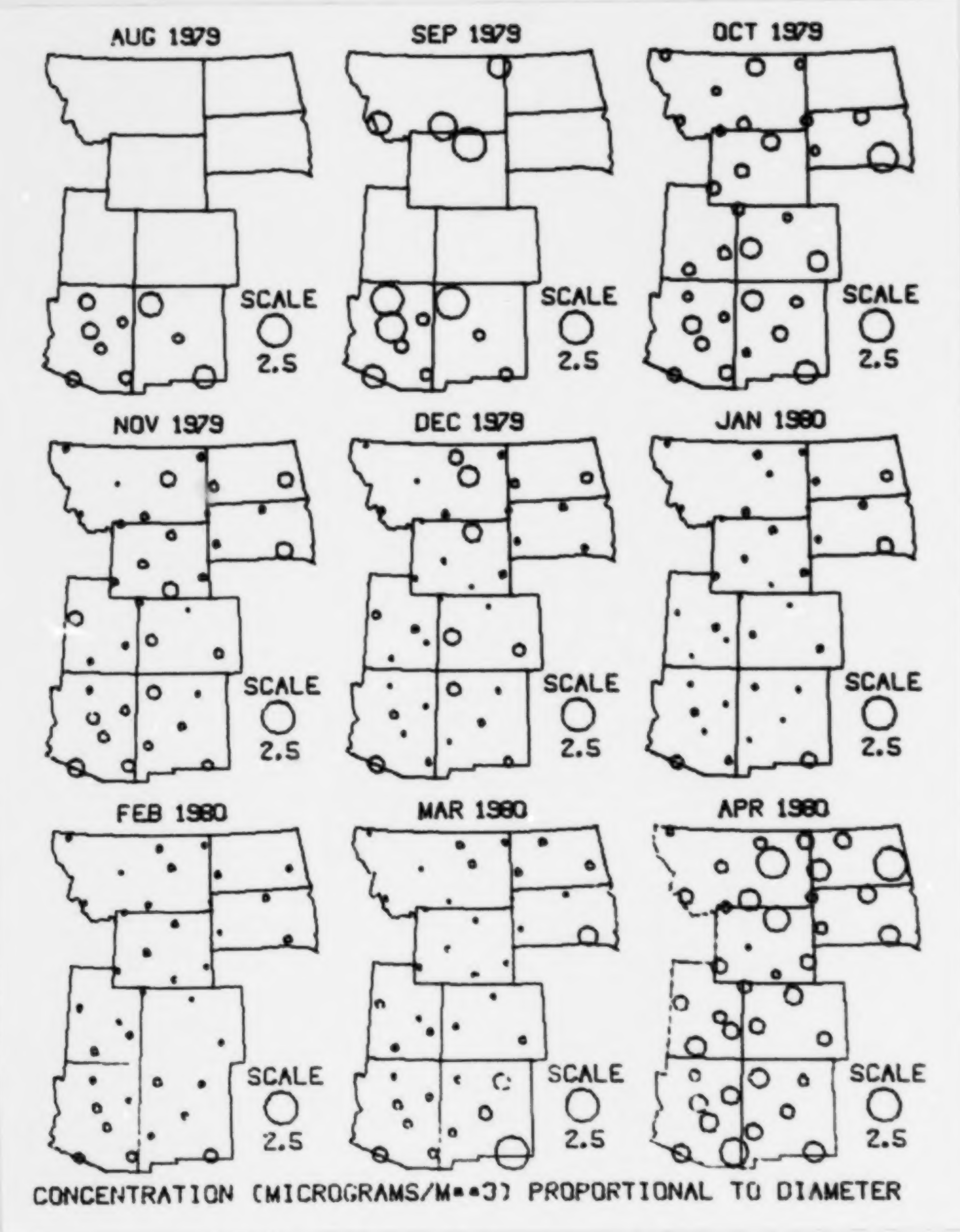
AUG 1979
SEP 1979
OCT 1979
NOV 1979
DEC 1979
JAN 1980
FEB 1980
MAR 1980
APR 1980
SCALE
2.5
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.10. Fine soil maps 8/79 - 4/80.

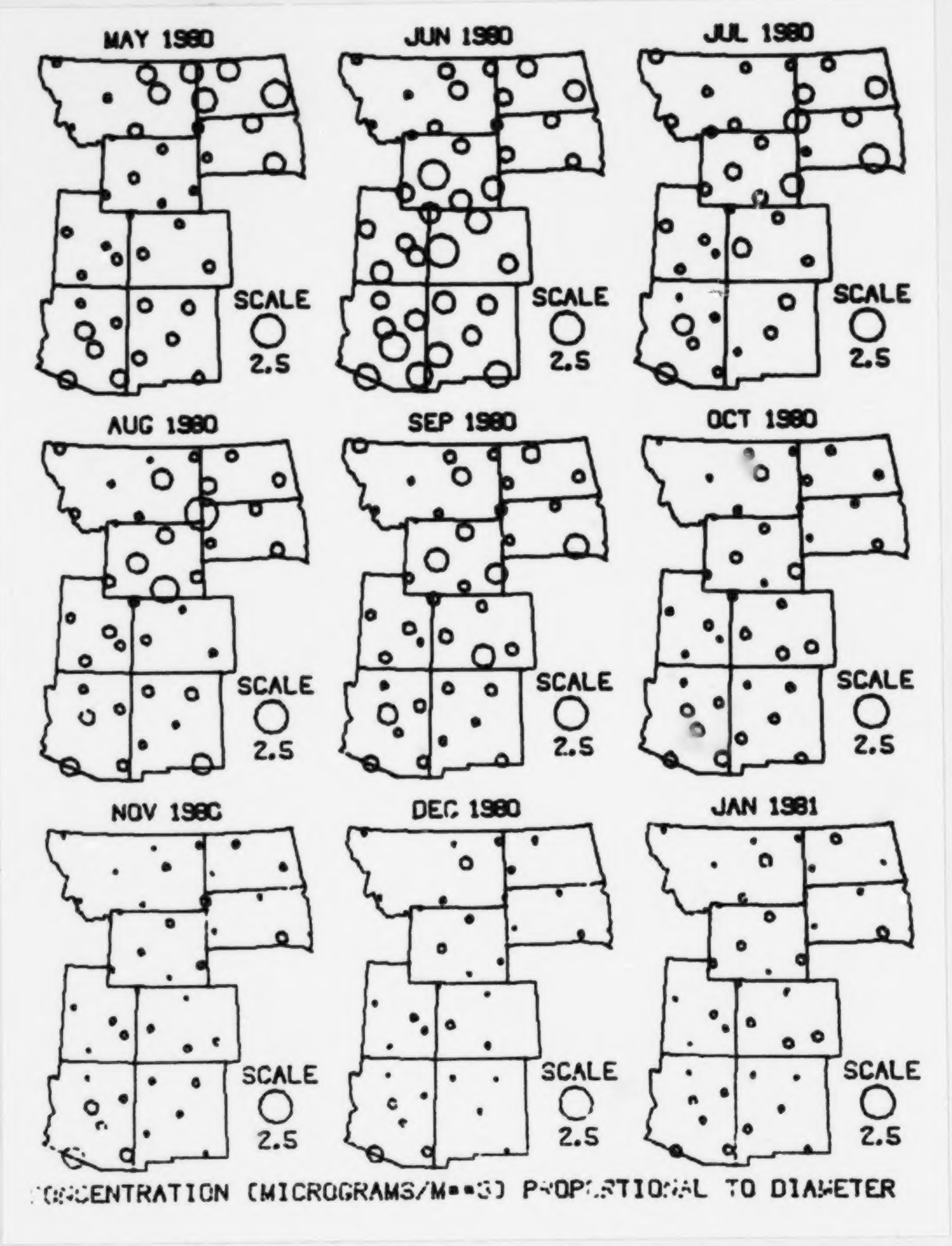
MAY 1980
JUN 1980
JUL 1980
SCALE
2.5
SCALE
2.5
SCALE
2.5
AUG 1980
SEP 1980
OCT 1980
SCALE
2.5
SCALE
2.5
SCALE
2.5
NOV 1980
DEC 1980
JAN 1981
SCALE
2.5
SCALE
2.5
SCALE
2.5
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.11. Fine soil maps 5/80 - 1/81.

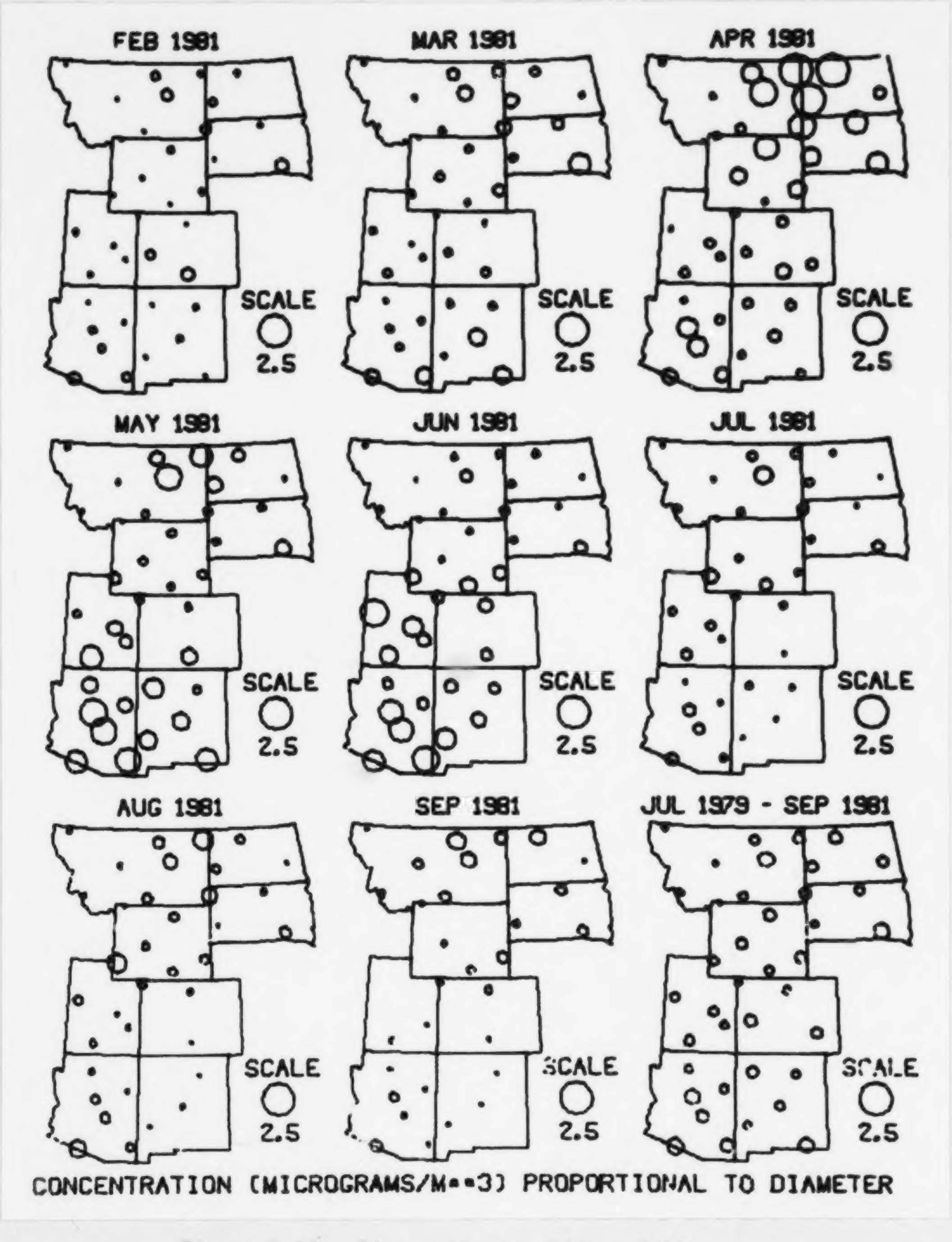
FEB 1981
MAR 1981
APR 1981
MAY 1981
JUN 1981
JUL 1981
AUG 1981
SEP 1981
JUL 1979 - SEP 1981
SCALE
2.5
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.12. Fine soil maps 2/81 - 9/81.

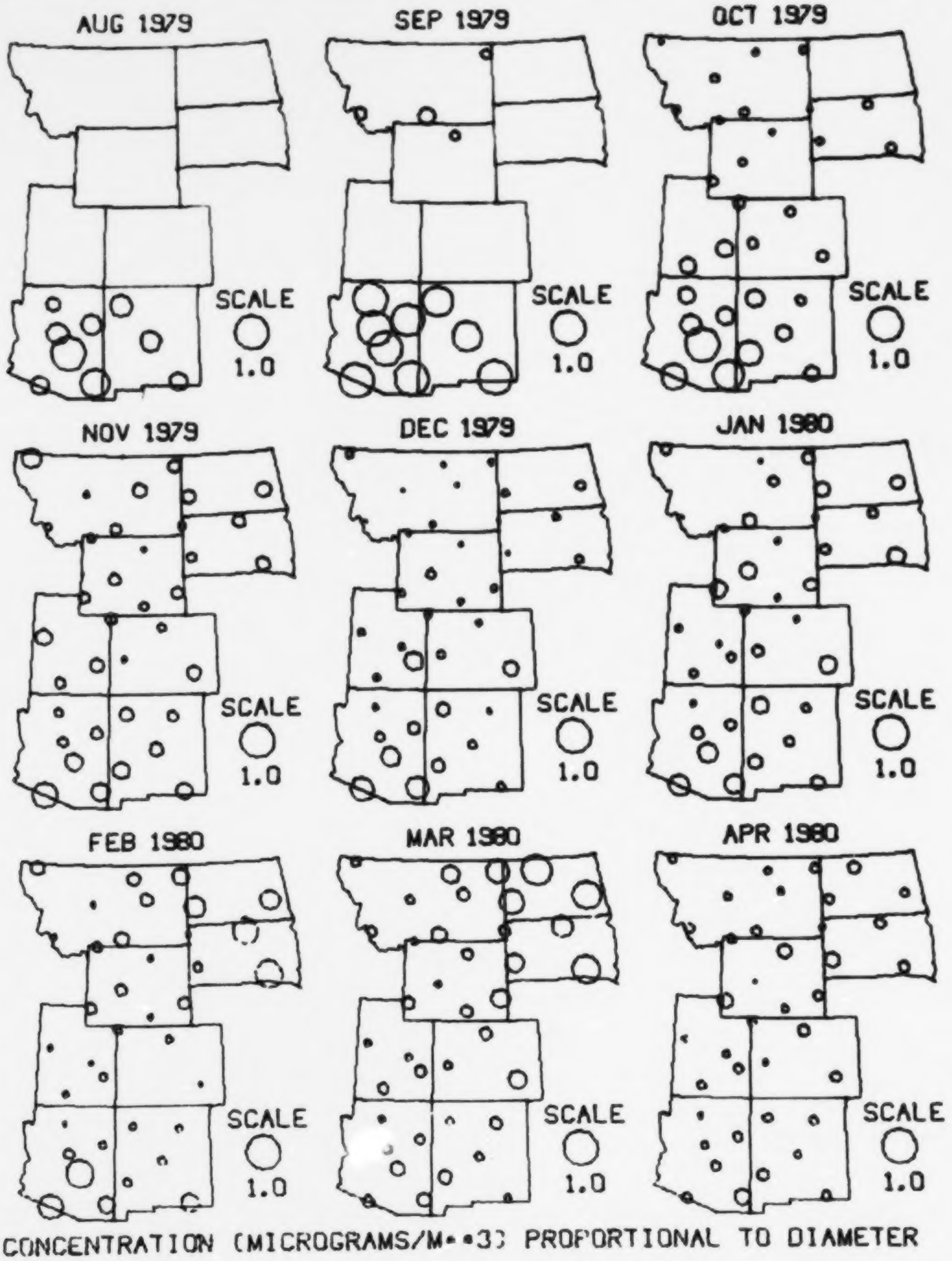
AUG 1979
SEP 1979
OCT 1979
NOV 1979
DEC 1979
JAN 1980
FEB 1980
MAR 1980
APR 1980
SCALE
1.0
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.13. Fine sulfur maps 8/79 - 4/80.

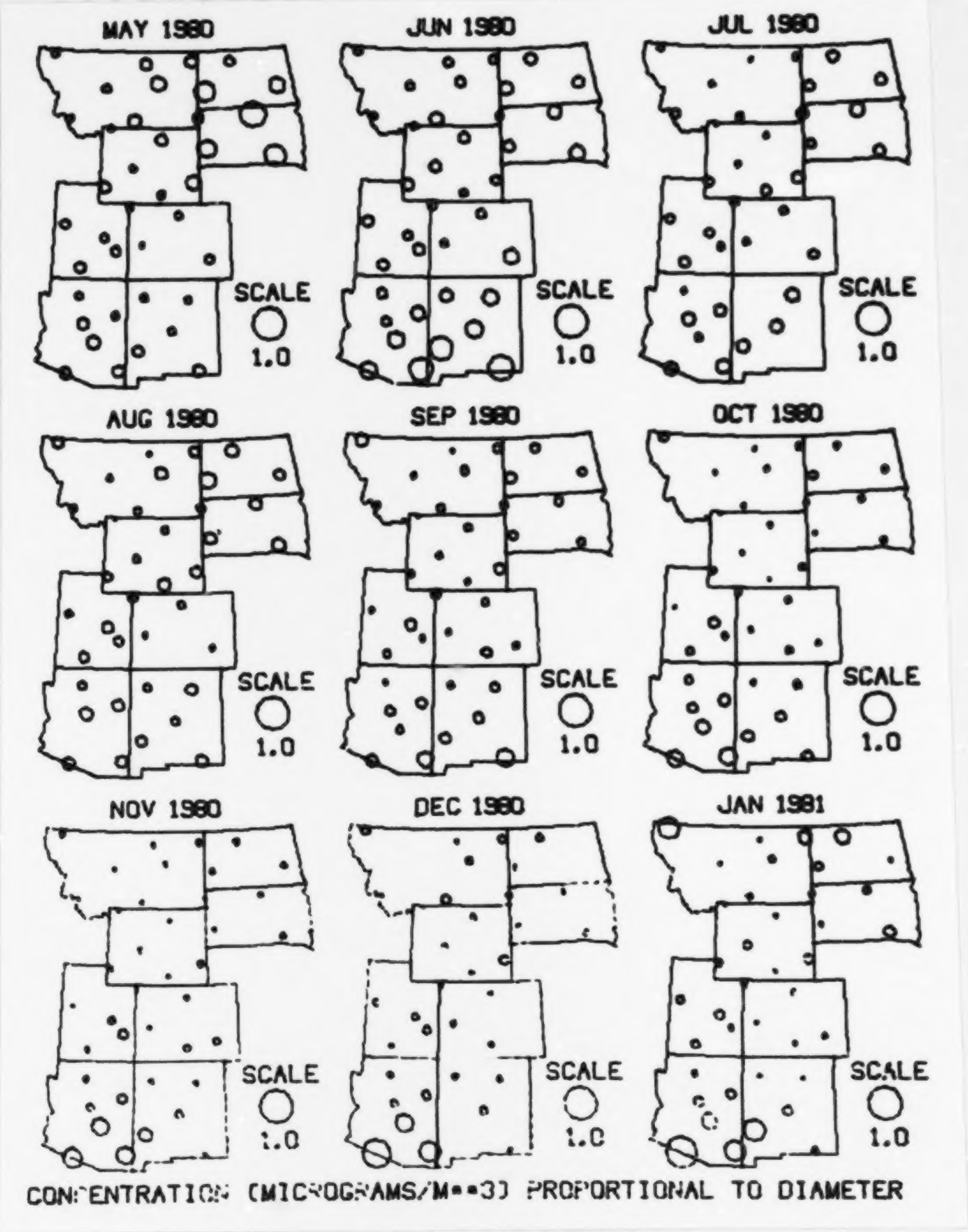
MAY 1980
JUN 1980
JUL 1980
AUG 1980
SEP 1980
OCT 1980
NOV 1980
DEC 1980
JAN 1981
SCALE
1.0
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.14. Fine sulfur maps 5/80 - 1/81.

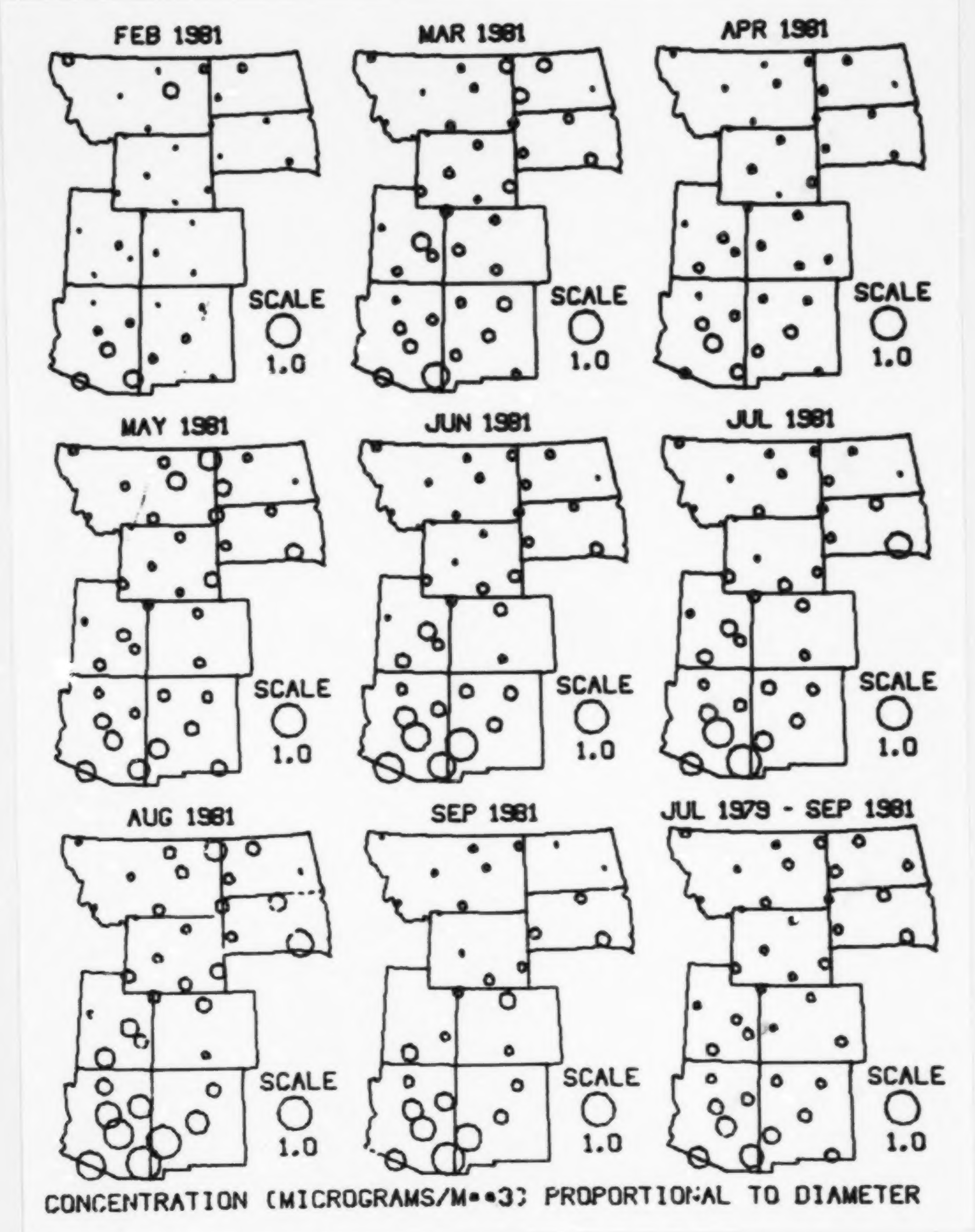
FEB 1981
MAR 1981
APR 1981
MAY 1981
JUN 1981
JUL 1981
AUG 1981
SEP 1981
JUL 1979 - SEP 1981
SCALE
1.0
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.15. Fine sulfur maps 2/81 - 9/81.

TABLE 3.5. FINE FRACTION OF TOTAL GRAVIMETRIC MASS

Site	Cases	Corr	Slope thru 0	Average Ratio	Ratio of Means
1	166	0.20	0.42 ± 0.04	0.56 ± 0.01	0.53 ± 0.03
2	175	0.53	0.22 ± 0.01	0.30 ± 0.01	0.26 ± 0.02
3	194	0.43	0.22 ± 0.01	0.40 ± 0.01	0.32 ± 0.02
4	140	0.31	0.17 ± 0.01	0.32 ± 0.01	0.26 ± 0.02
5	164	0.60	0.38 ± 0.01	0.44 ± 0.01	0.42 ± 0.02
6	173	0.24	0.15 ± 0.01	0.23 ± 0.01	0.19 ± 0.01
7	182	0.43	0.24 ± 0.01	0.38 ± 0.01	0.32 ± 0.02
8	156	0.48	0.18 ± 0.01	0.30 ± 0.01	0.24 ± 0.02
9	145	0.67	0.38 ± 0.01	0.47 ± 0.01	0.43 ± 0.02
10	196	0.56	0.27 ± 0.01	0.36 ± 0.01	0.32 ± 0.02
11	175	0.43	0.15 ± 0.01	0.26 ± 0.01	0.21 ± 0.02
12	195	0.41	0.22 ± 0.01	0.35 ± 0.01	0.30 ± 0.02
13	157	0.50	0.37 ± 0.02	0.44 ± 0.02	0.41 ± 0.02
14	159	0.28	0.08 ± 0.01	0.31 ± 0.01	0.25 ± 0.03
15	194	0.51	0.27 ± 0.01	0.41 ± 0.01	0.36 ± 0.02
16	194	0.20	0.20 ± 0.01	0.31 ± 0.01	0.27 ± 0.02
17	186	0.23	0.23 ± 0.02	0.34 ± 0.01	0.30 ± 0.02
18	197	0.29	0.24 ± 0.01	0.34 ± 0.01	0.30 ± 0.01
19	159	0.59	0.35 ± 0.01	0.42 ± 0.01	0.39 ± 0.02
20	167	0.73	0.31 ± 0.01	0.38 ± 0.01	0.34 ± 0.02
21	168	0.30	0.11 ± 0.01	0.37 ± 0.01	0.28 ± 0.03
22	186	0.47	0.32 ± 0.01	0.41 ± 0.01	0.37 ± 0.02
23	195	0.64	0.37 ± 0.01	0.46 ± 0.01	0.42 ± 0.02
24	157	0.52	0.31 ± 0.01	0.41 ± 0.01	0.37 ± 0.02
25	130	0.43	0.18 ± 0.01	0.33 ± 0.01	0.26 ± 0.02
26	122	0.18	0.28 ± 0.03	0.38 ± 0.02	0.35 ± 0.03
27	176	0.39	0.28 ± 0.02	0.46 ± 0.01	0.40 ± 0.02
28	195	0.45	0.32 ± 0.01	0.40 ± 0.01	0.37 ± 0.02
29	98	0.66	0.24 ± 0.01	0.34 ± 0.01	0.29 ± 0.02
30	181	0.30	0.33 ± 0.02	0.41 ± 0.01	0.39 ± 0.02
31	162	0.52	0.31 ± 0.01	0.36 ± 0.01	0.34 ± 0.02
32	185	0.60	0.35 ± 0.01	0.43 ± 0.01	0.39 ± 0.02
33	199	0.48	0.30 ± 0.01	0.36 ± 0.01	0.33 ± 0.01
34	187	0.51	0.40 ± 0.01	0.46 ± 0.01	0.43 ± 0.02
35	198	0.44	0.25 ± 0.01	0.40 ± 0.01	0.44 ± 0.02
36	197	0.35	0.28 ± 0.01	0.35 ± 0.01	0.33 ± 0.01
37	187	0.49	0.36 ± 0.01	0.43 ± 0.01	0.39 ± 0.01
38	150	0.64	0.41 ± 0.01	0.49 ± 0.01	0.46 ± 0.02
39	132	0.40	0.23 ± 0.02	0.36 ± 0.01	0.31 ± 0.02
40	192	0.53	0.33 ± 0.01	0.40 ± 0.01	0.37 ± 0.01
Average		0.45	0.28 ± 0.01	0.38 ± 0.01	0.34 ± 0.02

Fraction Fine = Fine / (Fine + Coarse).
Element must be found on both stages to be included.

TABLE 3.6. FINE FRACTION OF TOTAL SULFUR MASS

Site	Cases	Corr	Slope thru 0	Average Ratio	Ratio of Means
1	78	0.73	0.87 ± 0.01	0.87 ± 0.01	0.87 ± 0.02
2	51	0.48	0.89 ± 0.01	0.83 ± 0.02	0.86 ± 0.02
3	92	0.55	0.89 ± 0.01	0.86 ± 0.01	0.88 ± 0.01
4	74	0.51	0.88 ± 0.01	0.86 ± 0.01	0.87 ± 0.02
5	29	-0.08	0.89 ± 0.02	0.86 ± 0.02	0.87 ± 0.01
6	87	0.32	0.89 ± 0.01	0.83 ± 0.01	0.86 ± 0.02
7	91	0.43	0.91 ± 0.01	0.89 ± 0.01	0.90 ± 0.01
8	67	0.50	0.86 ± 0.02	0.89 ± 0.01	0.88 ± 0.03
9	32	0.60	0.89 ± 0.01	0.81 ± 0.02	0.86 ± 0.03
10	140	0.37	0.87 ± 0.01	0.82 ± 0.01	0.85 ± 0.01
11	43	0.49	0.88 ± 0.01	0.84 ± 0.02	0.87 ± 0.02
12	71	0.40	0.91 ± 0.01	0.87 ± 0.01	0.89 ± 0.01
13	31	0.43	0.85 ± 0.02	0.83 ± 0.02	0.85 ± 0.02
14	51	0.36	0.90 ± 0.01	0.88 ± 0.01	0.89 ± 0.01
15	87	0.26	0.92 ± 0.01	0.88 ± 0.01	0.90 ± 0.01
16	96	0.61	0.89 ± 0.01	0.87 ± 0.01	0.88 ± 0.01
17	52	0.44	0.88 ± 0.01	0.83 ± 0.02	0.86 ± 0.02
18	101	0.34	0.91 ± 0.01	0.89 ± 0.01	0.90 ± 0.01
19	79	0.59	0.89 ± 0.01	0.88 ± 0.01	0.89 ± 0.01
20	76	0.31	0.89 ± 0.01	0.84 ± 0.01	0.87 ± 0.01
21	69	0.02	0.73 ± 0.14	0.75 ± 0.03	0.73 ± 0.05
22	69	0.47	0.92 ± 0.01	0.89 ± 0.01	0.91 ± 0.01
23	69	0.36	0.93 ± 0.01	0.90 ± 0.01	0.91 ± 0.01
24	96	0.54	0.91 ± 0.01	0.89 ± 0.02	0.90 ± 0.01
25	05	0.08	0.80 ± 0.03	0.74 ± 0.01	0.75 ± 0.03
26	56	0.73	0.90 ± 0.01	0.89 ± 0.01	0.90 ± 0.01
27	69	0.31	0.93 ± 0.01	0.89 ± 0.01	0.91 ± 0.01
28	81	0.39	0.92 ± 0.01	0.89 ± 0.01	0.91 ± 0.01
29	34	-0.03	0.92 ± 0.01	0.91 ± 0.01	0.92 ± 0.01
30	62	0.29	0.92 ± 0.01	0.86 ± 0.01	0.89 ± 0.01
31	74	0.30	0.92 ± 0.01	0.88 ± 0.01	0.90 ± 0.01
32	70	0.26	0.93 ± 0.00	0.90 ± 0.01	0.92 ± 0.01
33	115	0.19	0.90 ± 0.01	0.87 ± 0.01	0.88 ± 0.01
34	101	0.18	0.93 ± 0.01	0.90 ± 0.01	0.92 ± 0.01
35	113	0.35	0.92 ± 0.00	0.90 ± 0.01	0.91 ± 0.01
36	117	0.32	0.88 ± 0.02	0.89 ± 0.01	0.88 ± 0.02
37	126	0.27	0.92 ± 0.01	0.90 ± 0.01	0.91 ± 0.01
38	100	0.30	0.92 ± 0.01	0.91 ± 0.01	0.91 ± 0.01
39	103	0.16	0.91 ± 0.01	0.85 ± 0.01	0.88 ± 0.01
40	144	0.55	0.93 ± 0.00	0.92 ± 0.00	0.93 ± 0.00
Average		0.37	0.89 ± 0.01	0.97 ± 0.01	0.88 ± 0.01

Fraction Fine = Fine / (Fine + Coarse).
Element must be found on both stages to be included.

TABLE 3.7. FINE FRACTION OF TOTAL IRON MASS

Site	Cases	Corr	Slope thru 0	Average Ratio	Ratio of Means
1	149	0.72	0.16 ± 0.01	0.22 ± 0.01	0.19 ± 0.02
2	165	0.81	0.12 ± 0.00	0.14 ± 0.00	0.13 ± 0.01
3	186	0.79	0.13 ± 0.00	0.17 ± 0.00	0.16 ± 0.02
4	131	0.54	0.12 ± 0.01	0.14 ± 0.01	0.13 ± 0.02
5	130	0.58	0.19 ± 0.01	0.22 ± 0.01	0.20 ± 0.02
6	172	0.54	0.10 ± 0.01	0.12 ± 0.00	0.12 ± 0.01
7	180	0.75	0.15 ± 0.00	0.19 ± 0.01	0.17 ± 0.01
8	143	0.85	0.10 ± 0.00	0.14 ± 0.01	0.11 ± 0.01
9	107	0.64	0.18 ± 0.01	0.26 ± 0.01	0.21 ± 0.03
10	189	0.76	0.15 ± 0.01	0.16 ± 0.01	0.15 ± 0.01
11	170	0.45	0.11 ± 0.01	0.14 ± 0.01	0.13 ± 0.02
12	189	0.84	0.12 ± 0.00	0.16 ± 0.01	0.14 ± 0.01
13	128	0.72	0.16 ± 0.01	0.23 ± 0.01	0.17 ± 0.02
14	162	0.68	0.13 ± 0.01	0.16 ± 0.01	0.15 ± 0.01
15	189	0.78	0.14 ± 0.00	0.20 ± 0.01	0.17 ± 0.02
16	195	0.53	0.12 ± 0.01	0.15 ± 0.01	0.14 ± 0.01
17	184	0.81	0.11 ± 0.00	0.14 ± 0.01	0.12 ± 0.01
18	197	0.80	0.14 ± 0.00	0.18 ± 0.00	0.16 ± 0.01
19	159	0.69	0.20 ± 0.01	0.23 ± 0.01	0.22 ± 0.01
20	151	0.78	0.18 ± 0.01	0.21 ± 0.01	0.20 ± 0.02
21	145	0.44	0.15 ± 0.01	0.24 ± 0.01	0.20 ± 0.02
22	170	0.74	0.17 ± 0.01	0.21 ± 0.01	0.18 ± 0.01
23	187	0.75	0.21 ± 0.01	0.21 ± 0.01	0.20 ± 0.02
24	148	0.74	0.21 ± 0.01	0.25 ± 0.01	0.23 ± 0.02
25	124	0.60	0.09 ± 0.01	0.14 ± 0.01	0.12 ± 0.01
26	119	0.65	0.15 ± 0.01	0.18 ± 0.01	0.17 ± 0.02
27	173	0.68	0.20 ± 0.01	0.27 ± 0.01	0.24 ± 0.02
28	179	0.77	0.20 ± 0.01	0.22 ± 0.01	0.21 ± 0.01
29	97	0.65	0.13 ± 0.01	0.18 ± 0.01	0.16 ± 0.02
30	165	0.79	0.19 ± 0.01	0.21 ± 0.01	0.20 ± 0.01
31	164	0.76	0.19 ± 0.01	0.19 ± 0.01	0.19 ± 0.01
32	176	0.68	0.18 ± 0.00	0.22 ± 0.01	0.20 ± 0.01
33	211	0.78	0.17 ± 0.00	0.18 ± 0.00	0.17 ± 0.01
34	197	0.70	0.19 ± 0.01	0.22 ± 0.01	0.21 ± 0.01
35	204	0.85	0.18 ± 0.00	0.22 ± 0.01	0.20 ± 0.01
36	209	0.62	0.14 ± 0.00	0.17 ± 0.00	0.16 ± 0.01
37	192	0.81	0.18 ± 0.00	0.19 ± 0.00	0.18 ± 0.01
38	147	0.70	0.21 ± 0.01	0.22 ± 0.01	0.21 ± 0.02
39	139	0.60	0.18 ± 0.01	0.21 ± 0.01	0.21 ± 0.02
40	202	0.69	0.19 ± 0.01	0.19 ± 0.01	0.19 ± 0.01
Average		0.70	0.16 ± 0.01	0.19 ± 0.01	0.18 ± 0.01

Fraction Fine = Fine / (Fine + Coarse).
Element must be found on both stages to be included.

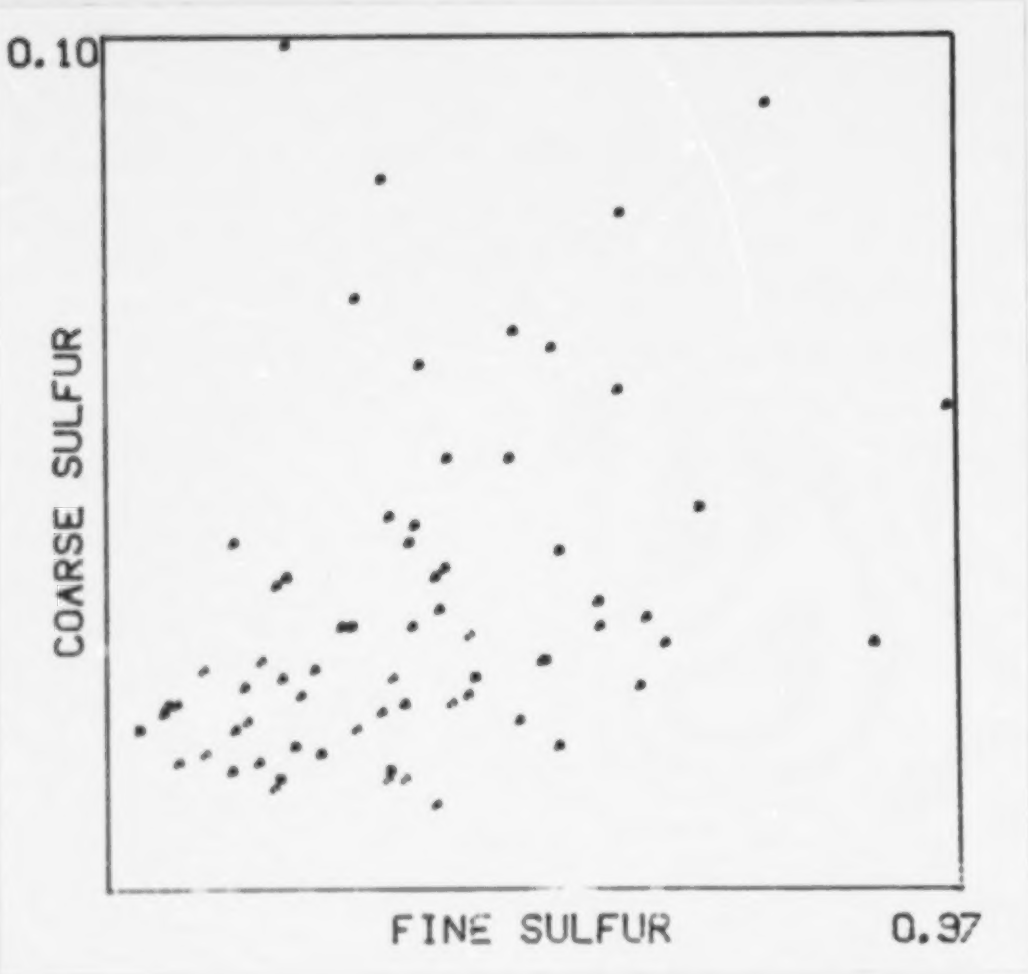

Figure 3.16. Scattergram comparison of coarse and fine sulfur.

TABLE 3.8. SOIL COMPOSITION - COMPARISON OF NETWORK AVERAGE TO AVERAGE ROCKS

	Ratios to Iron					
	Si/Fe	Al/Fe	Ca/Fe	K/Fe	Ti/Fe	S/Fe
Average Rock						
igneous	5.4	1.6	0.7	0.5	0.12	-
shale	5.8	1.7	0.5	0.6	0.08	0.11
sandstone	37.	2.6	4.0	1.1	0.15	0.06
limestone	6.4	1.1	80.	0.7	0.10	0.11
sediment	6.7	1.8	1.0	0.6	0.09	0.11
Network Average						
coarse	6.9	1.8	1.9	0.6	0.09	0.19
st. dev.	±1.5	±0.4	±0.9	±0.1	±0.02	±0.13
fine	7.2	2.2	1.8	0.9	0.09	-
st.dev.	±2.7	±0.5	±0.9	±0.3	±0.02	-

Calcium differed from the other elements in two ways. First, the network's Ca/Fe ratio was the only ratio that differed from that of sediment, with the network showing increased calcium. Second, the variation between sites, as measured by the value of the standard deviation relative to the mean, was 2.5 times greater for the calcium ratio than for the other ratios. The average ratios at each site were always much less than the 80 for limestone, rarely exceeding 5. A ratio of 5 would result if the soil were characterized by sediment with a 5% admixture of limestone. Figure 3.17 shows the correlation between calcium and iron at 6 sites. It is evident that the correlation at any given site was good, but that the slopes significantly differed even between nearby sites. This indicates that the soil particles are predominantly from a region smaller than the grid pattern of the network (about 100 km). The plots also show that the ratios for the fine stage were similar to those for the coarse stage. The map in Figure 3.18 shows the spatial distribution of the Ca/Fe ratio for the coarse stage. Most of the calcium-rich sites were clustered in the center of the network. Since this region does not have significant limestone deposits, this may reflect a calcium enriched sediment. The highest Ca/Fe ratio was at site 21, near the Great Salt Lake Desert.

Soil samples were collected at most sites, resuspended in the laboratory, and analyzed for elemental content (Cahill et al., 1981). The correlation between the Ca/Fe ratio measured in the air and the value measured in the resuspended soil sample is shown in Figure 3.19. The only anomaly occurred at Carlsbad Caverns, where the site is located on a limestone ridge, but the surrounding region is not limestone. The soil sample, from the limestone ridge, had considerably more calcium than the average aerosol. This indicates that the airborne soil particles tend to be from a region of at least several kilometers.

The composition of the coarse and fine soil-related elements at a given site were similar for all elements except potassium. From Table 3.8, the K/Fe ratio for the fine stage was 1.5 times that for the coarse stage. The differences between coarse and fine potassium can also be seen in the correlation plots of Figure 3.20. For the fine stage, there were many cases when the potassium values were well above the best-fitting line for the coarse stage, indicating enriched fine potassium. Figure 3.21 shows the distribution of ratios for each stage. For the coarse stage, the distribution was compact, while for the fine stage, the distribution was broader and shifted.

The excess fine potassium is probably due to smoke. Previous studies in the Willamette and Sacramento valleys, Lake Tahoe, and northern Arizona have shown elevated fine potassium concentrations during periods of known smoke episodes. However, the fraction of potassium in the smoke depends on the nature of the material being burned, ranging from 1% for nearby pine fires to 7% for hardwood fires. A fraction of 5% was obtained from field burning in the Willamette Valley (Lyons et al., 1980) and in a northern Arizona forest fire (Macias et al., 1981b). With a fraction of 5%, the smoke mass would account for approximately 10% of the total mass for the entire network, as shown in Figure 3.7.

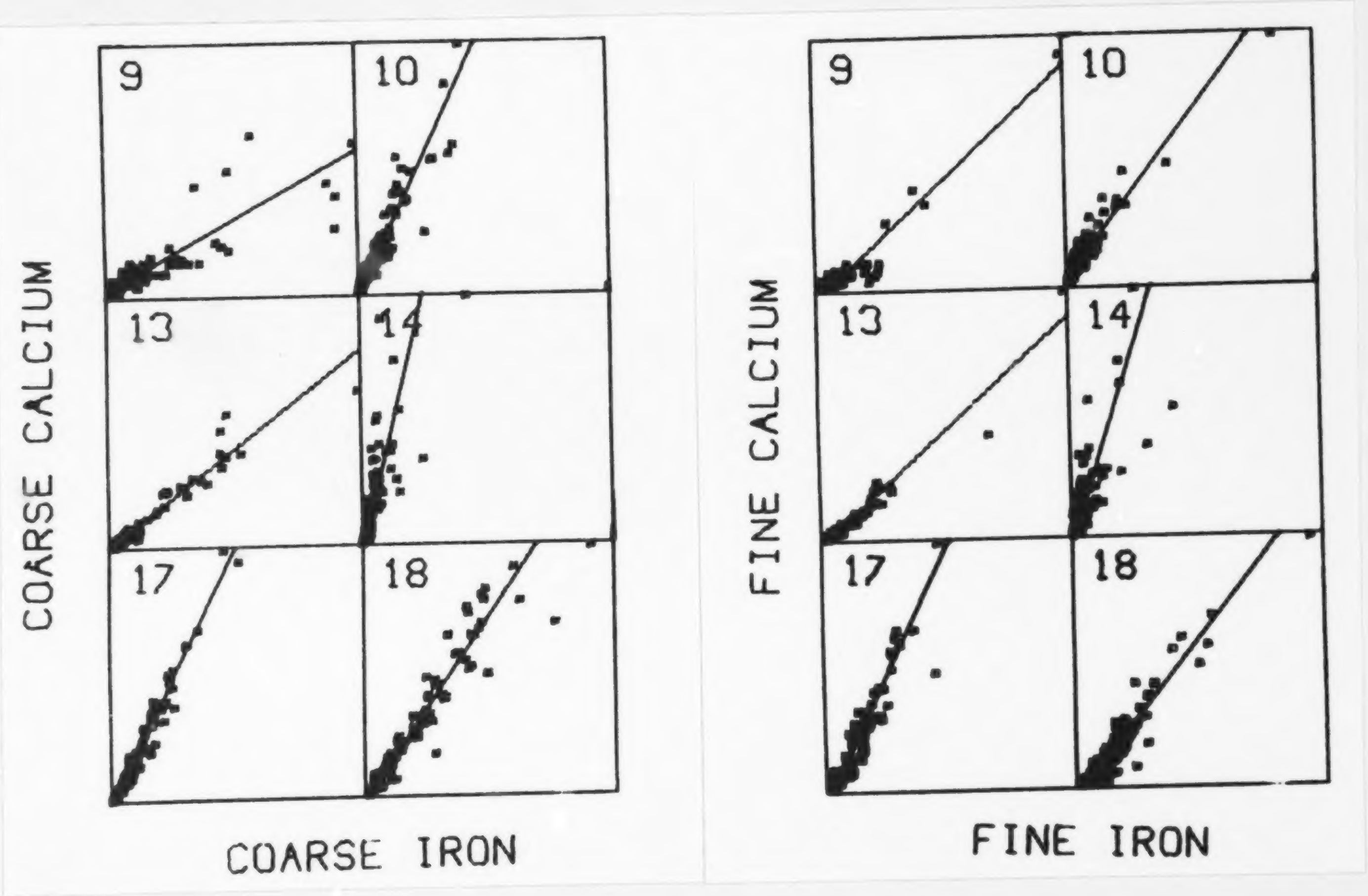

Figure 3.17. Scattergrams of coarse and fine iron for various sites.

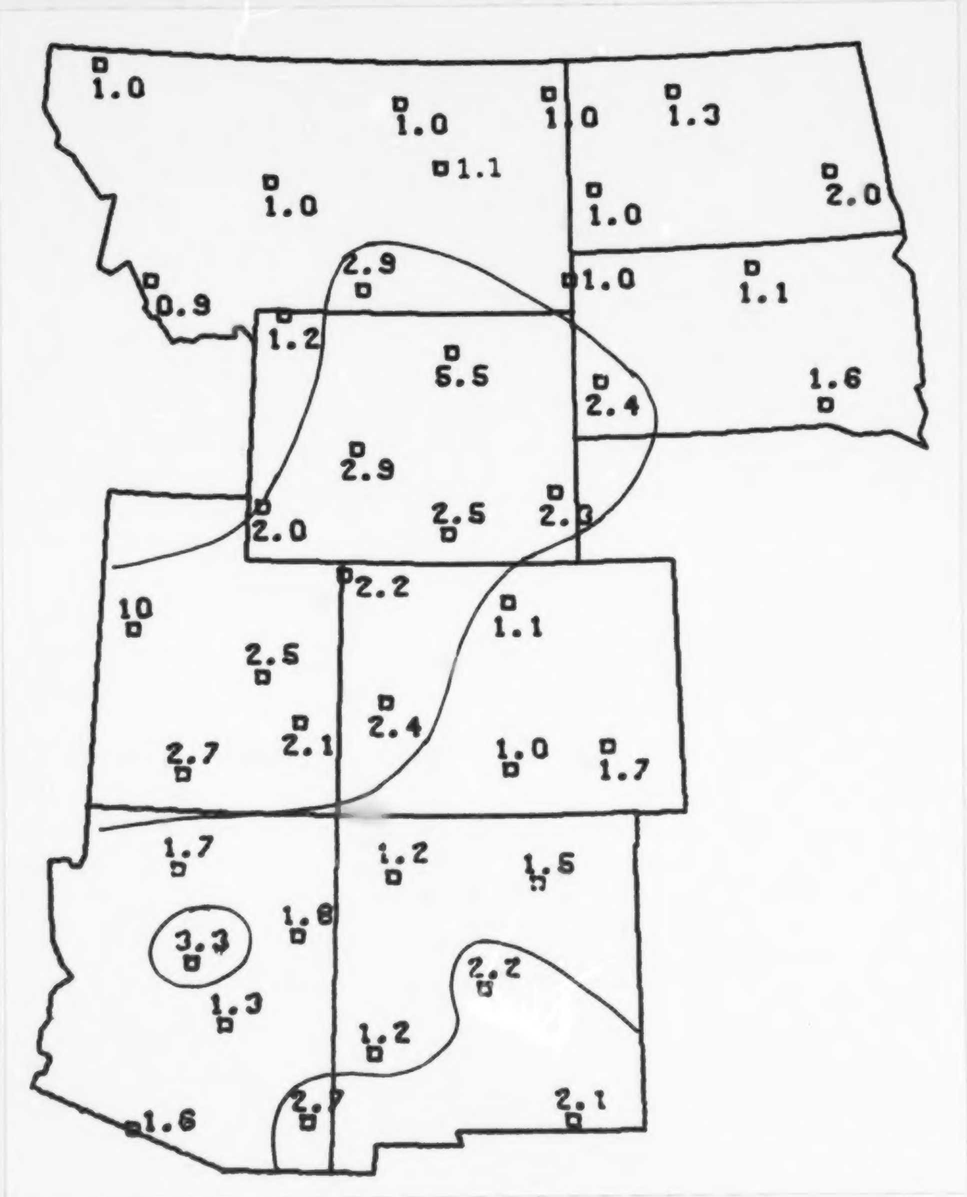
1.0
1.0
1.0
1.3
1.1
1.0
2.0
1.0
2.9
1.0
1.1
0.9
1.2
5.5
2.4
1.6
2.9
2.0
2.5
2.3
2.2
10
1.1
2.5
2.4
2.7
2.1
1.0
1.7
1.7
1.2
1.5
1.8
3.3
2.2
1.3
1.2
2.7
2.1
1.6

Figure 3.18. Coarse calcium/iron ratio map.

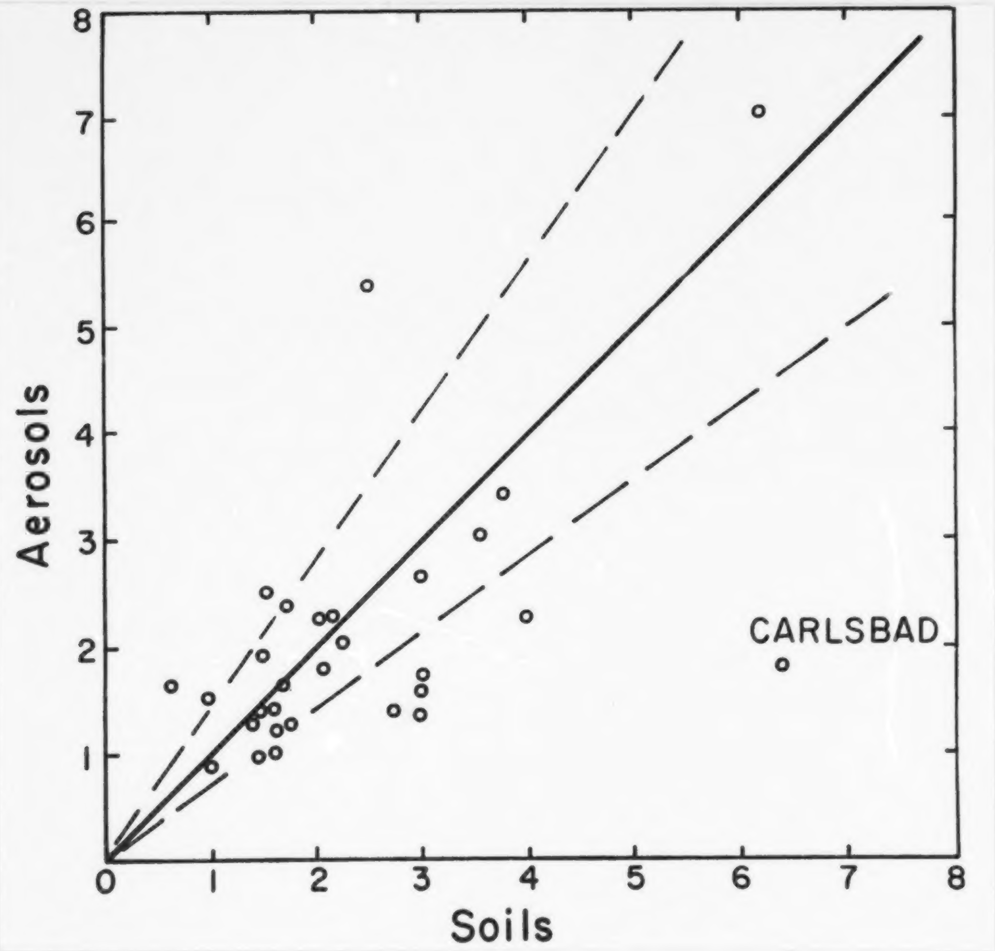

Figure 3.19. Scattergram comparison of aerosol and soil calcium/iron ratios.

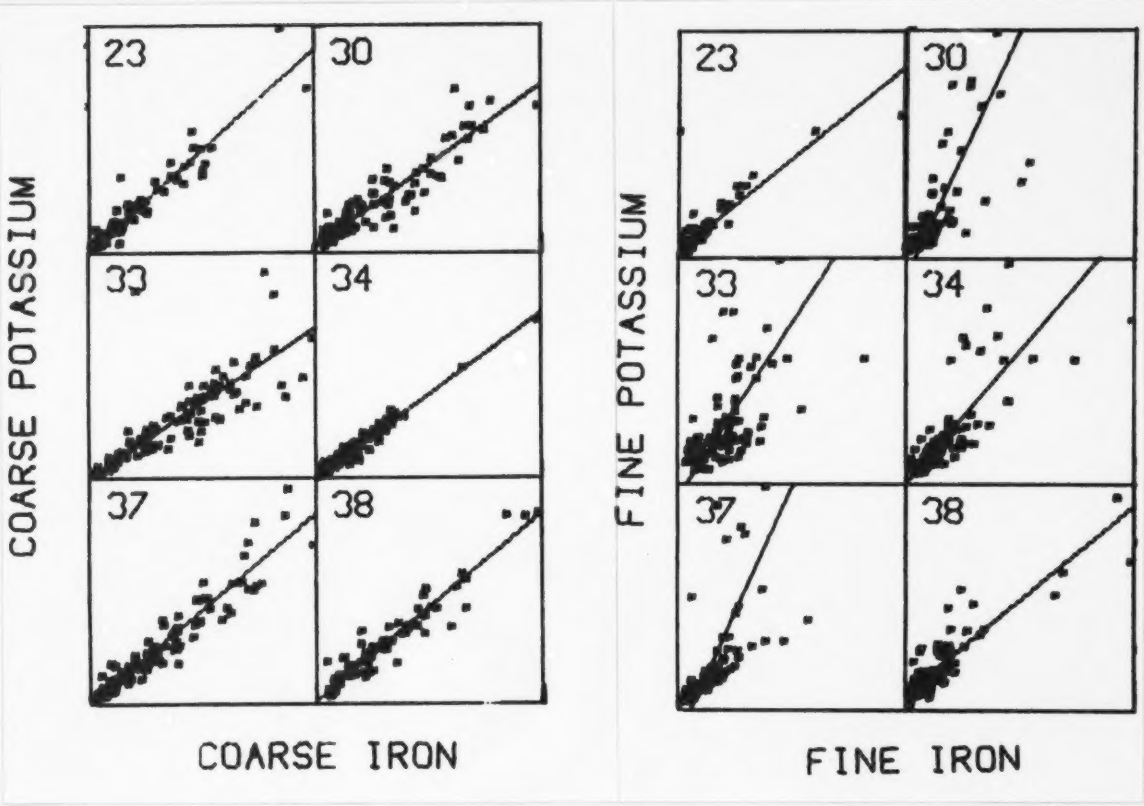

Figure 3.20. Scattergrams of potassium and iron for various sites.

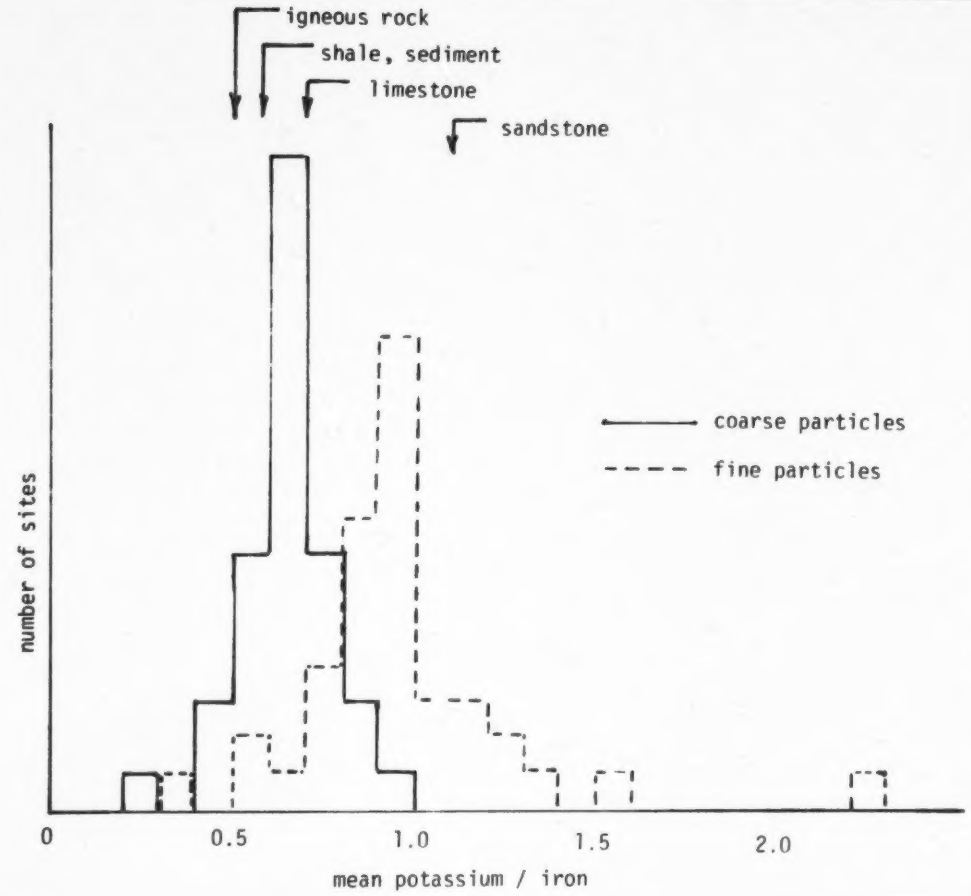

Figure 3.21. Distribution of potassium/iron ratios for coarse and fine particles.

The excess potassium (XSK) for a sample can be as calculated from the K/Fe ratio for coarse particles and the measured fine Fe concentration according to:

$$XSK = K_{fine} - Fe_{fine} \times (K/Fe)_{coarse}$$

The coarse K to Fe ratio was determined from the slope of the best-fitting line through the origin of coarse K versus coarse Fe. Time plots of excess potassium (Figure 3.22) show elevated values throughout the Arizona region during June of both 1980 and 1981. During these times winds were generally from the south in Arizona. This suggests that there may have been field burning in Mexico at the time. Figure 3.23 shows the spatial variation for both years combined.

OTHER ELEMENTS

Chlorine was found on a majority of coarse samples at sites 5, 21, and 36. For the 1981 data, the correlation coefficient between chlorine and sodium was 0.83 at site 36 and 0.94 at site 21, indicating that the chlorine was present as NaCl. Since site 36 is only 80 km from the Gulf of California, it is probable that this was due to marine air. Site 21, at the edge of the Great Salt Lake Desert, was characterized by unusually high concentrations of calcium, chlorine exceeding 10 μg/m^3. The chlorine here is evidently blowing salt. At site 5, it was not possible to determine the source of chlorine. Although routinely observed, the levels of chlorine were uniformly low, so that if the chlorine were present as NaCl, the sodium would have been below detection limits.

The lead concentrations at the remote sites were very low, rarely exceeding 100 ng/m^3. Lead was found on 40% to 60% of the samples at eight sites (6,17, 25,26,3 [illegible] 0). The presence of bromine on these samples would indicate an autom [illegible] Unfortunately, the bromine mass in automotive exhaust is arou [illegible] t of lead, so that the bromine levels would fall below the PIX [illegible] in many cases. At these sites, bromine is found on 14% to 50% [illegible] with lead. At sites 36, 37, and 40, the fraction is lowest, with [illegible] of the samples with lead also having bromine. This indicates that [illegible] sites are more likely to have a nonautomotive lead source. In this case the source is the group of copper smelters in southern Arizona (Eldred et al., 1982). At all eight sites, when lead and bromine were both found on a sample, the correlation coefficients were around 0.8, and the Br/Pb ratios were near 0.20. Sites 6, 17 and 25 were at small airports, while site 26 was at a small Air Force base. (However, sites 2 and 14, also at small airports, produced no high lead levels.) Site 33 was approximately one-half kilometer from Interstate 17. At site 26 there were also intercorrelations between fine zinc, lead and mass, and between coarse copper, lead, soil, and mass.

At site 39 there were high correlations between fine zinc, bromine and vanadium, although the number of pairs of samples was low. This was the only site at which fine vanadium was more common than coarse vanadium.

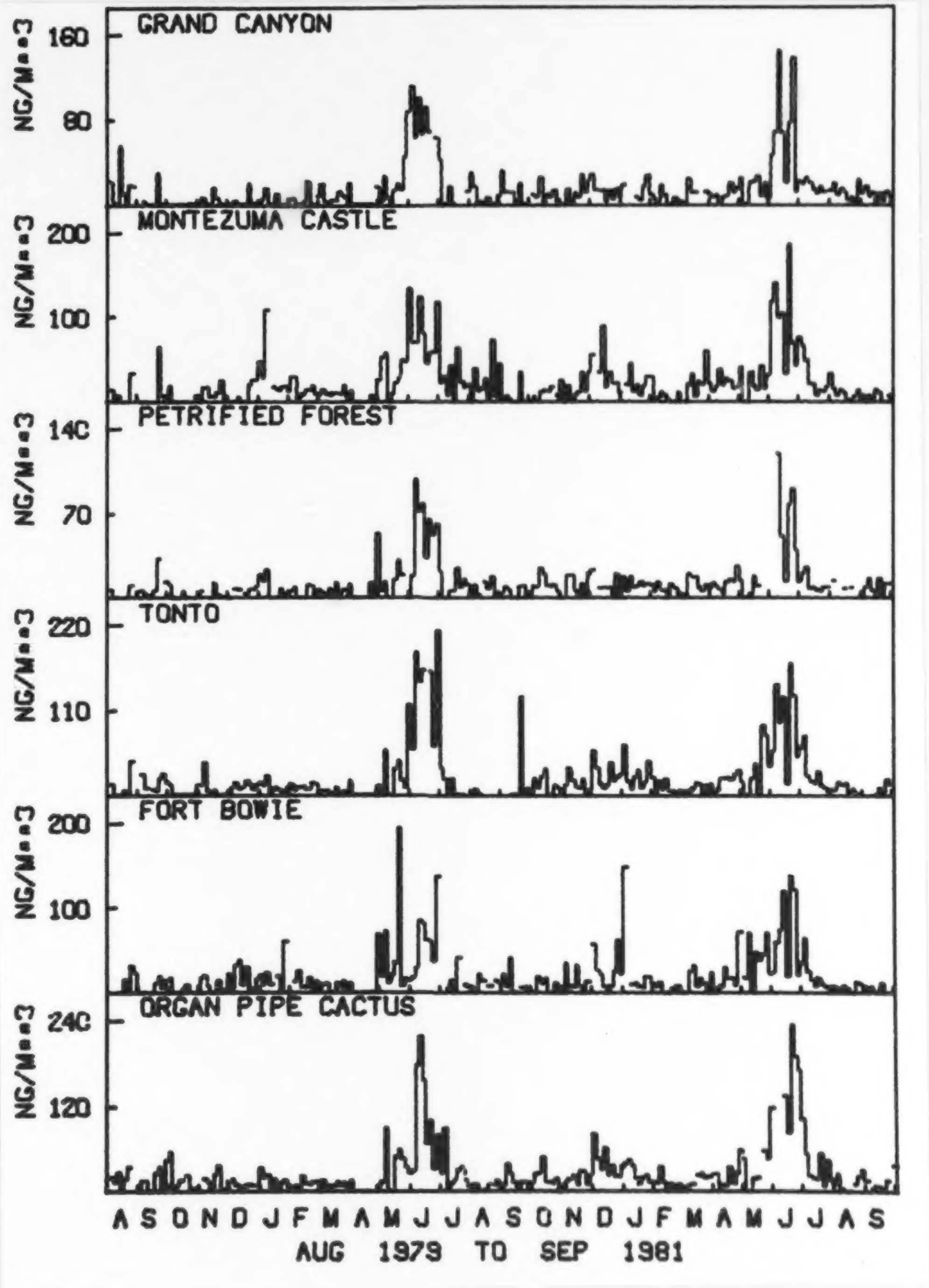

Figure 3.22. Excess fine potassium time plot.

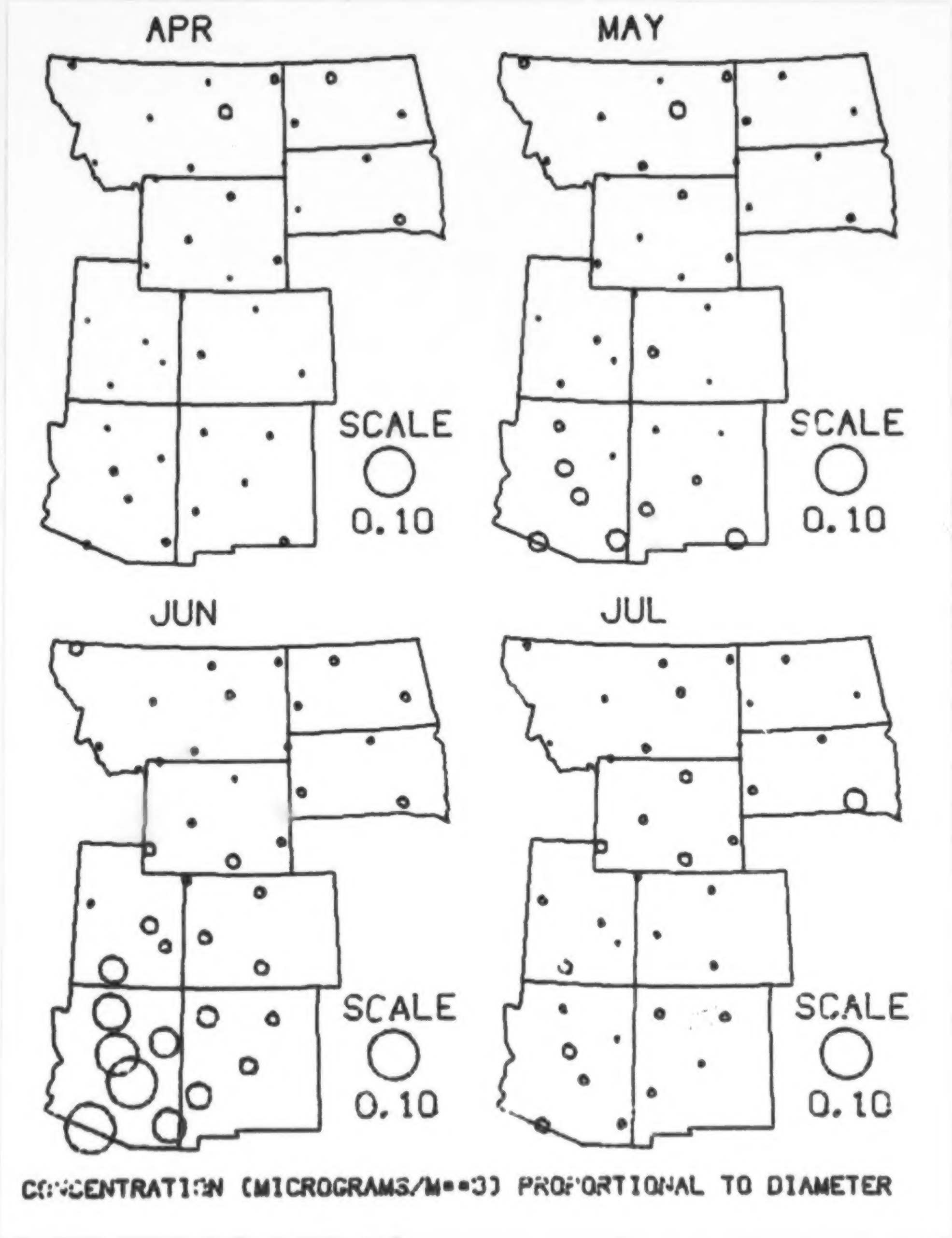
APR
MAY
SCALE
0.10
SCALE
0.10
JUN
JUL
SCALE
0.10
SCALE
0.10
CONCENTRATION (MICROGRAMS/M**3) PROPORTIONAL TO DIAMETER

Figure 3.23. Excess fine potassium maps.

Coarse copper and fine copper, zinc and lead were detected on a larger fraction of samples at the four sites in the region of the Arizona copper smelters (36, 37, 38, and 40), than at any other group of sites. At these sites, the elements intercorrelated with each other and with sulfur with correlation coefficients in a range of 0.6 to 0.8.

METEOROLOGY

Meteorological factors affecting particle concentrations in the network are actively being studied. In an effort to explore the nature of particle transport and to determine possible sources, work has been carried out on analysis of surface wind and transport fields, long-range trajectories, and diffusion model calculations.

Surface wind fields give insight into the general features of the flow patterns in the network states. Figures 3.24 to 3.26 show the monthly resultant vector average wind fields for the network for the period from August 1979 to July 1981. These fields were computed by averaging the wind vectors at each site for each 3-day sample period which began in the month indicated. The 3-day vectors were interpolated from National Weather Service sites. In the north, an eastward flow dominated in the fall and winter months. In spring and summer, occasional westward flows reduced or reversed the average eastward flow. Note in particular the westward flow in March and May, 1980, and in May and July, 1981. In the south, a northward flow prevailed overall though it varied from northwest to northeast. An annual variation in the wind field was not apparent as in the north. In general, however, the highest winds occurred in spring and summer, and the lowest winds occurred in winter. In March, May, and June of both 1980 and 1981, the winds were quite high and averaged from the southwest.

Figure 3.27 shows the vector average wind for August 1979 through July 1981. This map shows a resultant southerly flow at the southern U.S. border which persisted throughout Arizona and New Mexico. Near the southern border of Wyoming, the flow became westerly and continued westerly throughout Wyoming and Montana. In North and South Dakota, the flow varied from westerly to northerly.

Transport of fine sulfur has been calculated by taking the product of the sulfur concentration and the resultant wind during a sampling period. Mean northward flow in Arizona and New Mexico results in northward transport of fine sulfur because of large sources of sulfur at copper smelters in southern Arizona and New Mexico. At the Northern Great Plains sites occasional westward flow (opposite in direction to the mean eastward flow) can result in significant sulfur transport from sources to the east of the network.

A long range transport model (Heffter 1980) has been used for transport and diffusion calculations. Model calculations of sulfate concentrations have been made using simplified assumptions of SO_2 emissions from copper smelters in the south, SO_2 to sulfate conversion rates, and dry and wet deposition. These model calculations show that sulfate concentrations, resulting from copper smelter emissions, are of the same order of magnitude as the sulfate concentrations determined by measurements in the network.

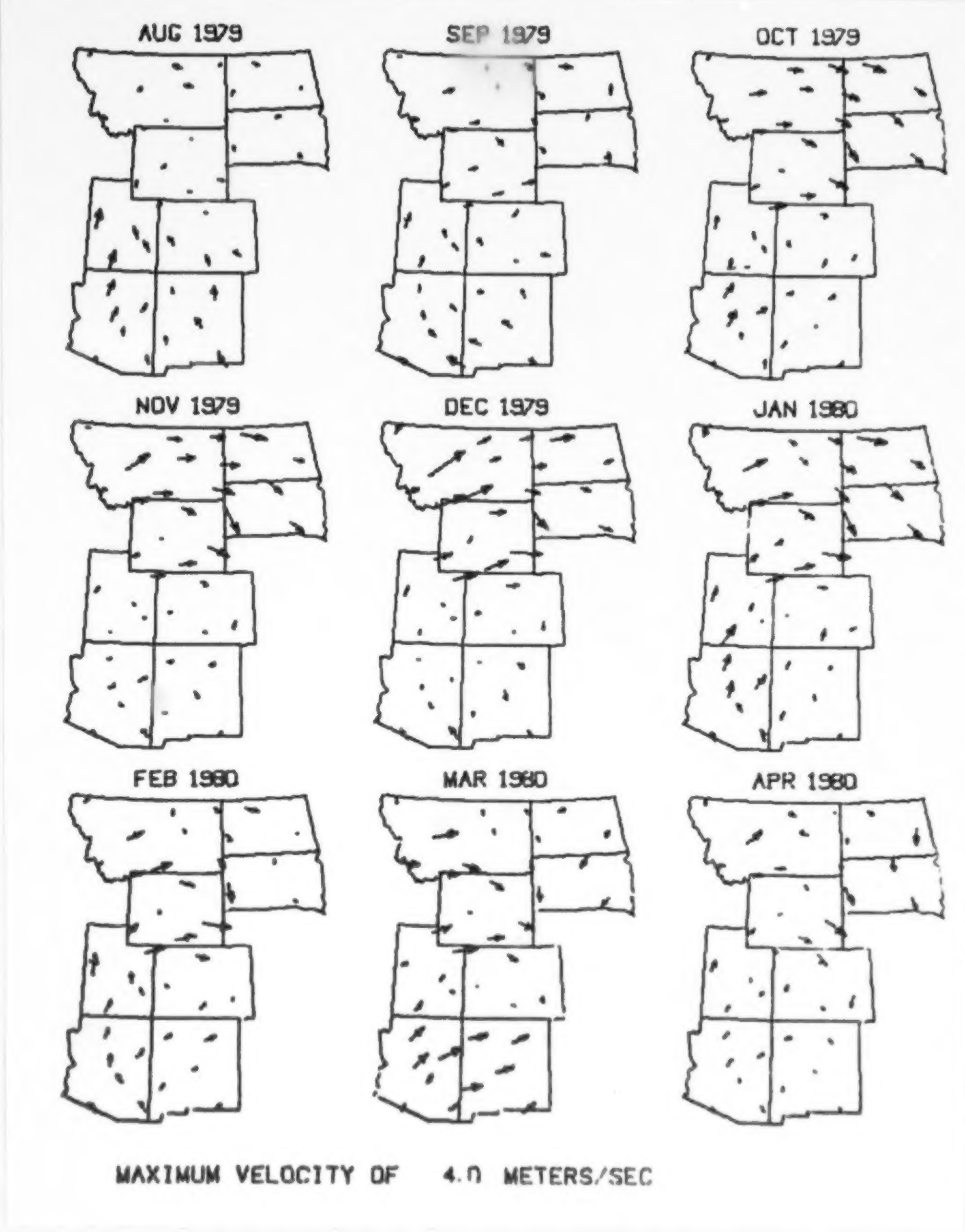
AUG 1979
SEP 1979
OCT 1979
NOV 1979
DEC 1979
JAN 1980
FEB 1980
MAR 1980
APR 1980
MAXIMUM VELOCITY OF 4.0 METERS/SEC

Figure 3.24. Three-day mean wind vector maps 8/79 - 4/80.

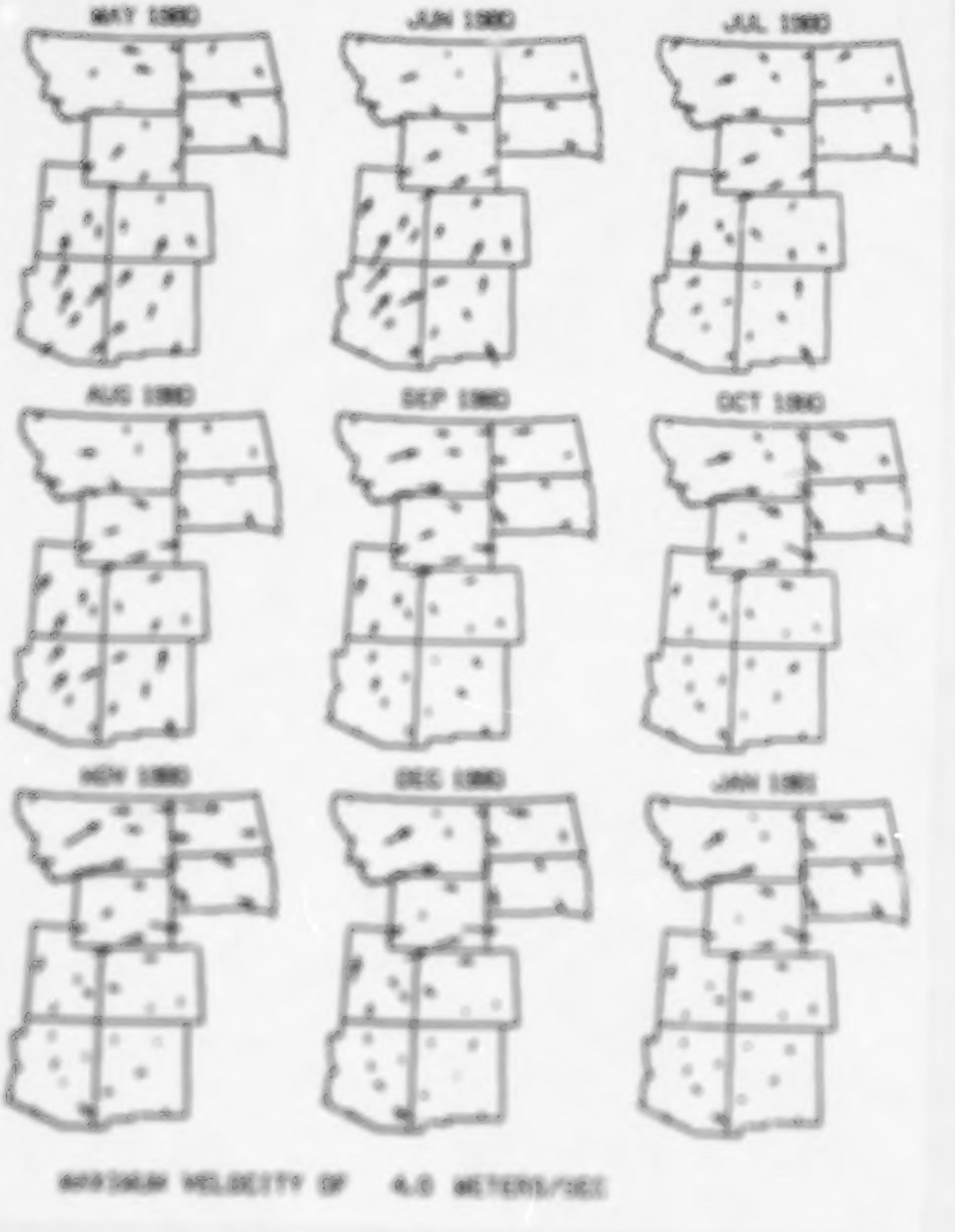
MAY 1980
JUN 1980
JUL 1980
AUG 1980
SEP 1980
OCT 1980
NOV 1980
DEC 1980
JAN 1981
MAXIMUM VELOCITY OF 4.0 METERS/SEC

Figure 3.25. Three-day mean wind vector maps 5/80 - 1/81.

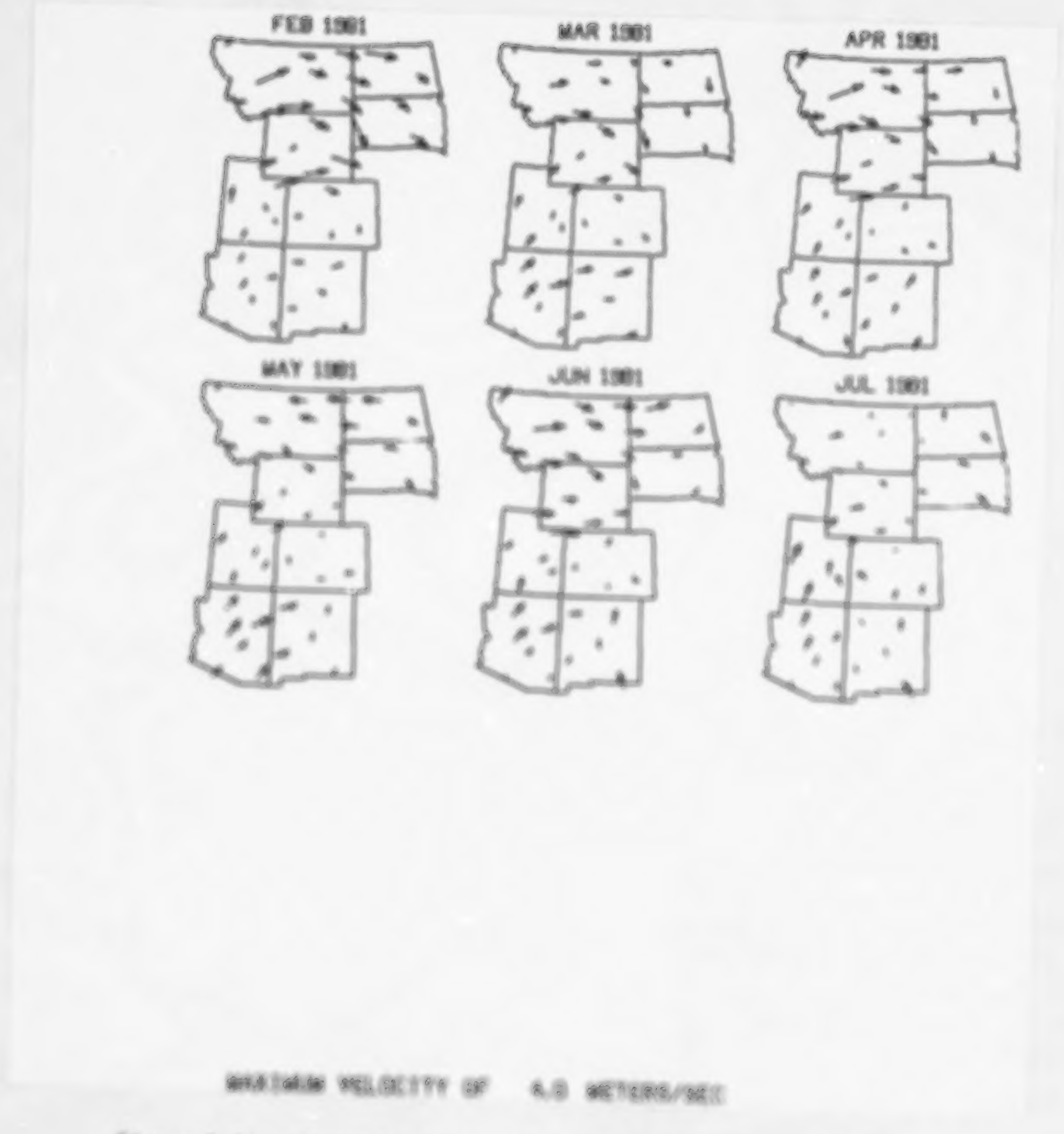
FEB 1981
MAR 1981
APR 1981
MAY 1981
JUN 1981
JUL 1981
MAXIMUM VELOCITY OF 4.0 METERS/SEC

Figure 3.26. Three-day mean wind vector maps 2/81 - 7/81.

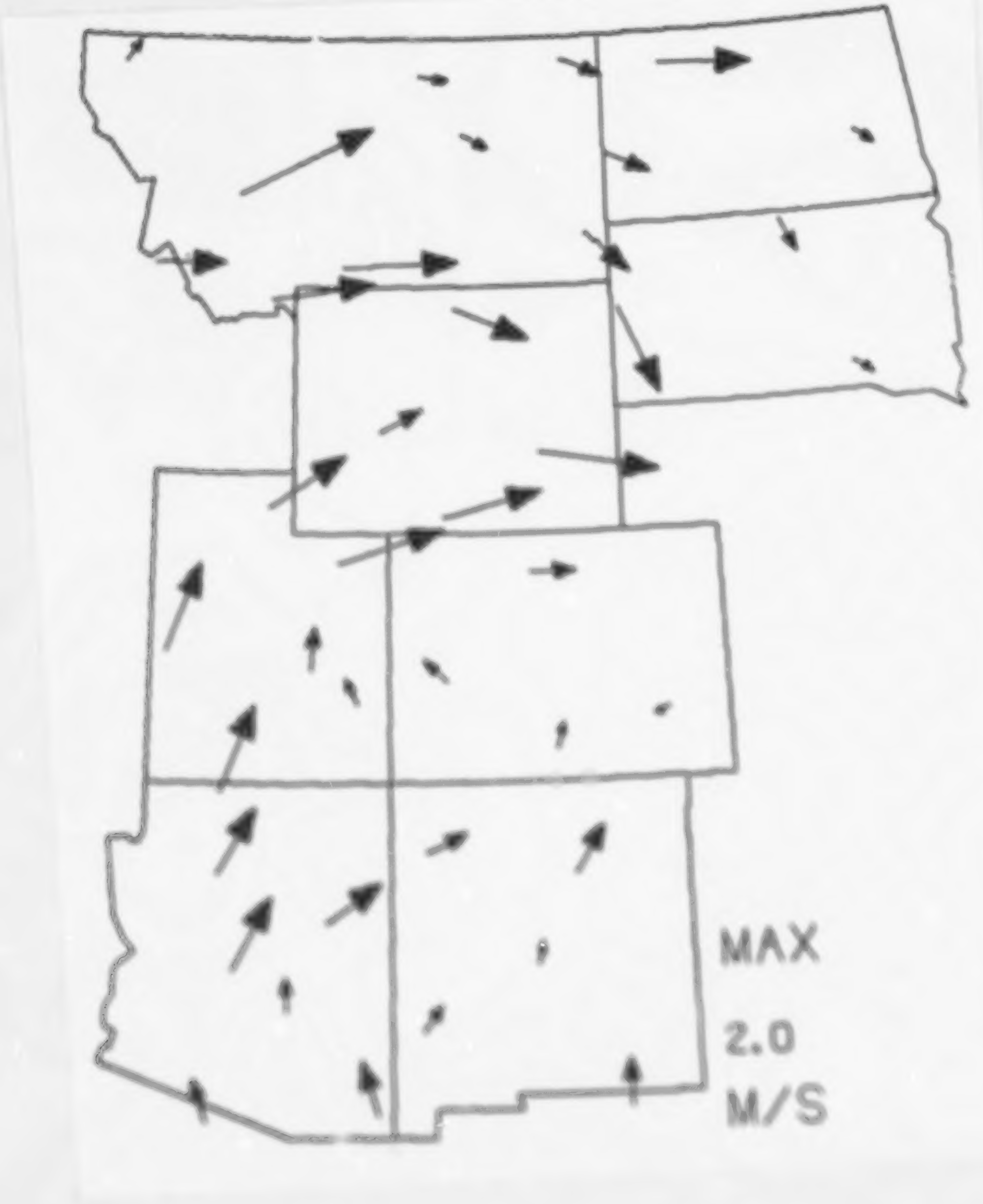

Figure 3.27. Three-day mean wind vector 6/79 - 7/81.

Additional work includes detailed trajectory analyses which indicate that periods of high sulfur at Grand Canyon National Park tended to be associated with slow transport and stagnation. Furthermore, during the summer of 1980 when most of the smelters in southern Arizona and New Mexico were not operating, high sulfur episodes at Grand Canyon were associated with trajectories coming from southern California.

ANNOTATED BIBLIOGRAPHY

Detailed interpretation of the data set gathered during this study lies beyond the scope of this report. However, there has been significant initial interpretation of these data. Considerable effort was expended in development of techniques of particle collection and elemental analysis and in the overall design of the network. Finally, several ancillary studies were conducted under this cooperative agreement. These efforts have resulted in numerous publications which are presented in this annotated bibliography. The publications are presented and discussed in the following four main sections:

- Techniques of Particle Collection and Analysis
- Design of the Network
- Ancillary Studies
- Early Interpretive Efforts

TECHNIQUES OF PARTICLE COLLECTION AND ANALYSIS

Early work in the program was centered on insuring accurate data from the network sites in terms of sampler performance, proton induced x-ray emission (PIXE) and gravimetric analyses. Later work resulted in extension of analytical techniques to the very light elements, hydrogen through fluorine, in order to match the sum of elements to the gravimetric mass. This was accomplished for the first time from a single sample collected in the Sacramento Valley. The role of agricultural smoke to visibility as studied in the Sacramento Valley by full elemental analyses has direct relevance to the role of forest fires in the intermountain region.

Samplers

Cahill, T. A. Innovative Aerosol Sampling Devices Based Upon PIXE Capabilities. Nuclear Instruments and Methods 181:473-480 (1981)

Cahill, T. A. Comments on Surface Coatings for Lundgren-Type Impactors. Aerosol Measurement, Dale A. Lundgren, Editor; University Presses of Florida. pp. 131-134 (1979).

Cahill, T. A. Size-Chemical Profiles of Environmental Samples by PIXE. American Nuclear Society. San Francisco (1981).

Gravimetric Analysis

Engelbrecht, D. R., T. A. Cahill and P. J. Feeney. Electrostatic Effects on Gravimetric Analysis of Membrane Filters. Journal of the Air Pollution Control Association. 30:391-392 (1980).

PIXE Analyses

Cahill, T. A. Sensitivity, Quality Assurance, and Cost in Automated Analysis via Ion Induced X-Rays. Nuclear Instruments and Methods 149:431-433 (1978).

Cahill, T. A. Proton Microprobes and Particle Induced X-Ray Analytical Systems. Annual Reviews Nuclear and Particle Science 30:211-252 (1980).

Cahill, T. A. Ion Beam Analysis of Environmental Samples. Symposium on Recent Developments in Biological and Chemical Research with Short Lived Radioisotopes; American Chemical Society Advances in Chemistry Series, Vol 197, pp 511-522.

Hill, M. W., L. D. Hansen, N. F. Mangelson, K. J. Faucette, D. J. Eatough, T. A. Cahill and B. Kusko. Measurement of Sample Temperatures Reached During Proton and Alpha Particle Irradiation of Thin PIXE Targets. Nuclear Instruments and Methods 181:69-70 (1981).

Cahill, T. A., R. G. Flocchini. Comments on Inaccuracies Encountered in Sulfur Determination by Particle Induced X-Ray Emission. Analytical Chemistry, Vol. 54, pp 1874-1877, (1982).

Analysis of Very Light Elements (hydrogen to flourine)

Cahill, T. A. Analysis of Very Light Elements in Aerosols. Los Angeles, CA. American Nuclear Society (1982).

Cahill, T. A., Y. Matsuda, B. H. Kusko. The Nature of Sacramento Valley Aerosols During Agricultural Burning. American Association for Aerosol Reseach, Santa Monica Meeting. (1982).

Cahill, T. A., Y. Matsuda, D. Shadon, R. A. Eldred, B. H. Kusko. Forward Alpha Scattering Techniques (FAST) for Element Hydrogen Through Florine, Nuclear Instruments and Methods, Accepted for Publication 6/83.

Cahill, T. A., R. A. Eldred, D. Shadon, P. J. Feeney, B. H. Kusko. Complete Elemental Analysis of Aerosals: PIXE, FAST, LIPM, Mass. Nuclear Instruments and Methods, Accepted for Publication 6/83.

DESIGN OF THE NETWORK

Due to the nature of the problem, the final design of the monitoring network was unlike that of any previous network in terms of the 6-day-in-7 sequence, the samplers, and the analysis. Two papers discuss the nature of the physical and financial constraints that led to the design.

Flocchini, R. G., T. A. Cahill, Lowell L. Ashbaugh, R. A. Eldred, P. J. Feeney and D. Shadoan. Regional Scale Synoptic Air Monitoring for Visibility Evaluation Based on PIXE Analyses. Nuclear Instruments and Methods 181:407-410 (1981).

Ashbaugh, L. L., J. B. Barone, T. A. Cahill, R. A. Eldred and R. G. The Influence of Synoptic Weather on the Distribution of Sulfur Aerosols in a Portion of the Western United States. (1980).

Ashbaugh, L. L., J. B. Barone, T. A. Cahill, R. A. Eldred and R. G. Flocchini. Characterization of Particle Episodes in the Arid West. Presented at the 74th annual meeting of the Air Pollution Control Association, paper 81-14a (1981).

ANCILLARY STUDIES

Several studies were performed within the umbrella of the cooperative agreement. The foremost of these was the EPA Visibility Impairment due to Sulfur Transport and Transformations in the Atmosphere (VISTTA) study from 1979 to 1981. It provided valuable testing of the equipment prior to deployment, showing equivalence of the stacked filter units, virtual impactors, and physical impactors. It also generated valuable early data on fine particles and visibility in Arizona and Utah.

The data from the early EPA funded studies of particles in Utah were a source of information which allowed the design of the network to proceed with good knowledge of both the levels of fine particles and the temporal variability of aerosols with synoptic weather. These data led to the 3-day integration period to maximize sensitivity, retain synoptic variability, generate excellent mean values, and minimize cost.

The Mt. St. Helen's eruption of May, 1980, provided a valuable by-product of the program, since the plume drifted across the network.

The visit of Dr. Wang Ming-Xing from Peiking and the presence of Prof. John Winchester at UCD for three months resulted in a study of dust storm profiles.

VISTTA Study

Macias, E. S., J. O. Zwicker, J. R. Ouimette, S. V. Hering, S. K. Friedlander, T. A. Cahill, G. A. Kuhlmey and L. W. Pichards. Regional Haze in the Southwestern U.S. Symposium on Plumes and Visibility, Grand Canyon, Arizona 1980. Atmospheric Environment 15:1971-1986 (1981).

Cahill, T. A., B. H. Kusko, L. L. Ashbaugh, J. B. Barone, R. A. Elred, and E. G. Walther. Regional and Local Determinations of Particulate Matter and Visibility in the Southwestern United States during June and July, 1979. Symposium on Plumes and Visibility, Grand Canyon 1980. Atmospheric Environment 15:2011-2016 (1981).

Ouimette, J. R., S. K. Friedlander, T. A. Cahill. Technique for Determining the Contributions of Aerosol Chemical Species to the Extinction Coefficient. Air Pollution Control Association Meeting. (1980).

Particle Sampling in Utah

Flocchini, R. G., T. A. Cahill, L. L. Ashbaugh, R. A. Eldred and M.

Pitchford. Seasonal Behavior of Particulate Matter at Three Rural Utah Sites. Atmospheric Environment 15:315-320 (1981).

Pitchford, M., R. G. Flocchini, R. G. Draftz, T. A. Cahill, L. L. Ashbaugh and R. A. Eldred. Silicon in Submicron Particles in the Southwest. Atmospheric Environment 15:321-333 (1981).

Cahill, T. A., and L. L. Ashbaugh. Size/Composition Profiles of Resuspended Fly Ash. Environmental and Climatic Impact of Coal Utilization. J. J. Singh and A. Deepak, Editors; Academic Press. pp. 569-573 (1980).

Mt. St. Helens

Cahill, T. A., J. B. Barone, B. Kusko, L. L. Ashbaugh. Size-Composition Profiles of Airborne Fine Particulate Matter from Mt. St. Helens. American Geophysical Union Fall Meeting. (1980).

Leifer, R., L. Hinchliffe, I. Fisenne, H. Franklin, E. Knutson, M. Olden, W. Sedlacek, E. Mroz, and T. Cahill. Measurements of the Stratospheric Plume from the Mt. St. Helens Eruption Radioactivity and Chemical Composition. Science 214:904-907 (1981).

Dust Storms

Ming-Xing, W., J. W. Winchester, T. A. Cahill, R. Lixin. Chemical Elemental Composition of Wind Blown Dust Beijing, April 1980. Dexue Tongbao (Science Bulletin), Vol 27, pp. 1193-1199 (1981).

EARLY INTERPRETIVE EFFORTS

The earliest interpretive efforts were primarily descriptive. They were hampered by the partial data set available when they were conducted. More recent work has the benefit of the full data set allowing more robust statistical, case study and trend analysis techniques.

Cahill, T. A., R. A. Eldred, R. G. Flocchini, M. Pitchford. Size/Composition Signatures of Fine Soil Aerosols in the Western United States. ACS Hawaii, April (1979).

Cahill, T. A., L. L. Ashbaugh, R. A. Eldred, P. J. Feeney, B. Kusko and R. G. Flocchini. Comparisons between Size-Segreated Resuspended Soil Samples and Ambient Aerosols in the Western United States. AMS Meeting. Las Vegas, Nevada (1981).

Eldred, R. A., J. B. Barone, L. L. Ashbaugh, M. Pitchford. Characterization of Atmospheric Particulate Concentrations in the Western Fine Particle Network (1980).

Ashbaugh, L. L., J. B. Barone, R. A. Eldred, L. O. Myrup and R. G. Flocchini. The Influence of Synoptic Weather on the Distribution of Sulfur Aerosols in a Portion of the Western United States. (1980).

Flocchini, R. F., T. A. Cahill, M. L. Pitchford, R. A. Eldred, P. J. Feeney, and L. L. Ashbaugh. Characterization of Particles in the Arid West. Atmospheric Environment 15:2017-2030 (1981). Symposium on Plumes and Visibility, Grand Canyon, Arizona. Atmospheric Environment 15:2017-2030 (1981).

Pitchford, A., M. Pitchford, W. Malm, R. G. Flocchini, T. A. Cahill and E. Walther. Regional Analysis of Factors Affecting Visual Air Quality. Symposium on Plumes and Visibility, Grand Canyon, Arizona 1980. Atmospheric Environment 15:2043-2054 (1981).

Pitchford, M. The Relationship of Regional Visibility to Coarse and Fine Particle Concentration in the Southwest. J. Air Pollution Control Association 32:814-821 (1982).

Eldred, R. A., L. L. Ashbaugh, R. G. Flocchini, L. O. Myrup and M. C. Pitchford. Effect of the 1980 Copper Smelter Strike on Southwestern Ambient Aerosols. American Association for Aerosol Research (AAAR) Santa Monica, CA (1982).

Eldred, R. A., L. L. Ashbaugh, T. A. Cahill, R. G. Flocchini. Sulfate Levels in the Southwest During the 1980 Copper Smelter Strike. J. Air Pollution Control Association 33:110-113 (1982).

LITERATURE CITED

Barone, J. B., L. L. Ashbaugh, B. H. Kusko, and T. A. Cahill. 1980. The effects of Owens Dry Lake on air quality in the Owens Valley with Implications for the Mono Lake area. Atmospheric Aerosol: Source/Air Quality Relationships. E. S. Macias and P. K. Hopke, editors. ACS Symposium Series. Vol. 167, pp. 327-346 (1981).

Cahill, T. A., R. G. Flocchini, R. A. Eldred, P. J. Feeney, S. Lange, D. Shadoan, and G. Wolfe. Monitoring of Smog Aerosols with Elemental Analysis by Accelerator Beams. Proceedings of the 17th Materials Research Symposium. National Bureau of Standards, Maryland. (1976).

Cahill, T. A., L. L. Ashbaugh, J. B. Barone, R. A. Eldred, P. J. Feeney, R. G. Flocchini, C. Goodart, D. J. Shadoan, and G. W. Wolfe. Analysis of Respirable Fractions in Atmospheric Particulates via Sequential Filtration. APCA Journal 27:675-678. (1978a).

Cahill, T. A., R. A. Eldred, J. Barone, and L. L. Ashbaugh. Ambient Aerosol Sampling with Stacked Filter Units, Federal Highway Administration, RD-78-178, 1978. (1978b).

Cahill, T. A., L. L. Ashbaugh, R. A. Eldred, P. J. Feeney, . . H. Kusko and R. G. Flocchini. Comparisons between Size-Segregrated Resuspended Soil Samples and Ambient Aerosols in the Western United States, Atmospheric Aerosol: Source/Air Quality Relationships, E. S. Macias and P. K. Hopke, Editors; American Chemical Society. Symposium Series, Vol. 167, pp. 269-285. (1981).

Camp, D. C., A. L. Van Lehn, B. W. Loo. Intercomparison of Samplers Used in the Determination of Aerosol Composition. EPA 600/7-78-118. (1978).

Camp, D. C., A. L., Van Lehn, T. J., Rhodes, A. H. Pradzynski. Intercomparison of Trace Element Determinations in Symulated and Real Air Particulate Samples X-Ray Spectrometry. Vol. 4 pp. 123-137 (1975).

Dzubay, T. G., N. Morosoff, G. L. Whitaker, H. Yasuda. Evaluation of Polymer Films as Standards for X-Ray Fluorescence Spectrometers, Submitted to Electron Microscopy and X-Ray Applications to Environmental and Occupational Health Analysis, Vol. 3, Ann Arbor Science Publishers. (1981).

Eldred, R. A., L. L. Ashbaugh, T. A. Cahill, R. G. Flocchini, and M. L. Pitchford, Sulfate Levels in the Southwest During the 1980 Copper Smelter Strike, Journal of the Air Pollution Control Association. Vol. 33, pp. 110-113. (1983).

Engelbrecht, D. R., T. A. Cahill and P. J. Feeney. Electrostatic Effects on Gravimetric Analysis of Membrane Filters. Air Pollution Control Association Journal 30:391-392. (1981).

Flocchini, R. G., T. A. Cahill, D. J. Shadoan, S. J. Lange, R. A. Eldred, P. J. Feeney, G. W. Wolfe, D. C. Simmeroth, and J. K. Suder. Monitoring California's Aerosols by Size and Elemental Composition. Environmental Science and Technology 10:76-82. (1976).

Flocchini, R. G., T. A. Cahill, L. L. Ashbaugh, R. A. Eldred and M. Pitchford. Seasonal Behavior of Particulate Matter at Three Rural Utah sites. Atmospheric Environment. 15:315-320. (1980).

Flocchini, R. G., T. A. Cahill, P. J. Feeney, and D. J. Shadoan. Western Energy Resource Development Area Fine Particulate Characterization Study Sites, EPA Report No. 600-4-81 March 1981.

Harrison, J. and R. A. Eldred. Data Acquisition and Reduction for Elemental Analysis of Aerosol Samples. Advances in X-Ray Anal. 17, 560. (1973).

Heffter, J. L. (1980) Air Resources Laboratories Atmospheric Transport and Dispersion Model (ARL-ATAD). NOAA Technical Memorandum ERLARL-81, Air Resources Laboratories, Silver Spring, Maryland, 20910. 17 pp.

Hidy, G. M., B. R. Appel, R. J. Charlson W. E. Clark, S. K. Friedlander, D. H. Hutchinson, T. B. Smith, J. Suder, J. J. Wesolvwski and K. T. Whitby (1975), Summary of the California Aerosol Characterization Experiment, J. Air. Poll. Control Assoc. 25, 1106-1114.

John, W. AIHL, Berkeley, Report to the California Air Resources Board, and Private Communication. (1980).

Loo, B. W., J. M. Jaklevic and F. S. Goulding. Dichotomous Virtual Impactors for Large Scale Monitoring of Airbone Particulate Matter.

Lyons, C. E., I. Tombach, R. A. Eldred, ad J. E. Core. Relating Particulate Matter Sources and Impacts in the Wilamette Valley During Field and Slash Burning, Procceedings of the 72nd Anual Meeting of the Air Pollution Control Association, Paper 79-46.3.1. (1980.

Macias, E. S., J. O. Zwicker, J. R. Ouimete, S. V. Hering, S. K. Friedlander, T. A. Cahill, G. A. Kuhlmey, L. W. Rchards. Regional Haze Case Studies in the Southwestern U.S.-I Aerosol Cemical Composition, Atmospheric Environment 15:1971. (1981a).

Macias, E. S., J. O. Zwicker, W. H. White Regional Haze Case Studies in the Southwestern U.S.-II Source Contribuions, Atmospheric Environment 15:1987. (1981b).

Rhodes, J. R. and C. B. Hunter. Particle Size Effects in X-Ray Emission Analysis: Simplified Formulae for Crtain Practical Cases. X-Ray Spectrometry 1 (1972) 113.

Stevens, R. K. and T. G. Dzubay. Recent Developments in Air Particulate Monitoring. Proceedings on Instrumental Methods for Air and Water Measurements and Monitoring. IEEE Transactins on Nuclear Science. (1975).

Stevens, R. K. and T. G. Dzubay. Dichotomous Sampler - A Practical Approach to Fractionation and Collection. EPA -600/2-78-112 (1978).

APPENDIX A

PERSONNEL AND PROJECT ORGANIZATION

TABLE A-1. PROJECT PERSONNEL

Name	Affiliation	Grant funded FTE/yr (Total/yr)	Responsibilities
Thomas A. Cahill, Ph.D.	Physics Dept.	0.12 (0.4)	Principal Investigator Analytical Techniques Soils;Special Studies
Robert G. Flocchini, Ph.D.	Land, Air Water Resources	0.12 (0.3)	Principal Investigator Project Manager; Aerosol Characterization
Robert A. Eldred, Ph.D.	Air Quality Group (AQG); Crocker Nuclear Lab (CNL)	1.0	Investigator; Head of Data Analysis, Reduction Handling,Statistical Associations
Patrick J. Feeney, M.S.	AQG, CNL	1.0	Manager of Network Operations; Sampling Instrumentation; Selection
Dan J. Shadoan, M.S.	AQG, CNL	0.3	X-Ray Fluorescence; Sampling Instrumentation, Non-Standard Samples
Lowell L. Ashbaugh, M.S. Ph.D.	AQG, CNL	1.0	Head of Quality Assurance Meteorological Analyses, Trajectories, Sulfur Fine Particle Transport

TABLE A-1. (Continued)

Name	Affiliation	Grant funded FTE/yr (Total/yr)	Responsibilities
John J. Barone, Ph.D	AQG, CNL	0.2	Statistical Methods, Airborne Techniques, Remote Sampling.
Bruce Kusko, M.S. (Ph.D. Candidate)	AQG, Physics	0.2	Sample Analysis; VISTTA Program.
David Englebrecht, B.S.	AQG, CNL (to 8/1/80)	1.0	Head of Sample Handling; Gravimetric Analysis
John Olivera, B.S.	AQG, CNL	1.0	Replaces D. Englebrecht
Monica Echaves, Student	AQG, CNL	0.5	Sample Handling.
Robert Pimental, Student	AQG, CNL	0.5	Sample Handling.
Andrew McFarland, Ph.D.	Texas AM	Contract	Inlet Tests
Wang Ming Xing, Ph.D.	Academica Sinica, China	(2 wks)	Dust Sampling in Remote Areas.
John Winchester, Ph.D.	Florida State	(3 mos)	Sulfur Chemistry
Yatsuda Matsuda, D. Eng.	Osaka Prefecture	(8 mos)	Sulfur Chemistry; Aerosol Characterization

TABLE A-2. COOPERATING SCIENTISTS

Name	Affiliation	Project Component
David Johnson	USGS, Menlo Park	Mount St. Helens, general
Andre Sarna-Wojicki	USGS, Menlo Park	Mount St. Helens, general
Ray Wilcox	USGS, Denver	Mount St. Helens, general
Robert Leifer	DOE, New York	Mount St. Helens, U2 flight
Peter Hobbs	Univ. of Washington	Mount St. Helens, B-23 flights.
Paul Hammond	Portland State Univ.	Mount St. Helens, ground based samples
Bob Sidle	Foundation Sciences	Mount St. Helens, ground based samples
Lee Hansen	Brigham Young Univ.	Sulfur analyses with PIXE, beam temperature measurements
Mike Darzi	Florida State Univ.	Remote analyses/volcanoes
Andy Andreae	Florida State Univ.	Remote C analyses
Alistaire Leslie	Florida State Univ.	Streaker sampling/WFPN
Kin Coulson	NOAA, Mauna Loa	Remote S sampling Observatory
Peter McMurray	Univ. of Minnesota	VISTTA sampling
Will Richards	MRI	VISTTA sampling
Berndt Simoneit	UCLA	(planned) Analyses of organic material
Leonard O. Myrup	UCD	Transport; wind trajectory

TABLE A-3. COOPERATING AGENCIES

National Park Service

U.S. Forest Service

U.S. Fish and Wildlife Service

Bureau of Land Management

PROJECT ORGANIZATION

The organizational chart for the program is shown in Figure A-1. The job description for each position and its associated responsibilities are outlined below.

I. PROJECT MANAGER

A. Basic Function:

The Project Manager is responsible to the principal investigator for all aspects of the program, with emphasis on maintaining communications between the EPA and all group members and monitoring financial matters.

B. Responsibilities and Authorities:

1. Maintains communications with EPA project supervisor.
2. Supervises communications with all members of the project, normally through weekly meetings and agenda items.
3. Monitors all expenditures on the program, working with management and accounting at Crocker Nuclear Laboratory.
4. Oversees publication of results, working with the principal investigators.
5. Represents the principal investigators at meetings and conferences.

II. NETWORK OPERATIONS SUPERVISOR

A. Basic Function:

The network operations supervisor is responsible for all aspects of the program bearing upon the collection of samples from network sites, up to the transfer of the samples to the Analytical Supervisor for analysis.

B. Responsibilities and Authorities:

1. Oversees the acquisition and maintenance of all equipment and supplies associated with sample collection, including air samplers, flow devices and sampling substrates.
2. Evaluates all equipment prior to placement in the field, including side by side tests, flow calibration, etc.
3. Oversees site selection, draws up siting criteria, trains field operators, maintains communication with field personnel.
4. Coordinates all aspects of sample handling, including handling of substrates and return of flow data and information about environmental conditions from field observers.

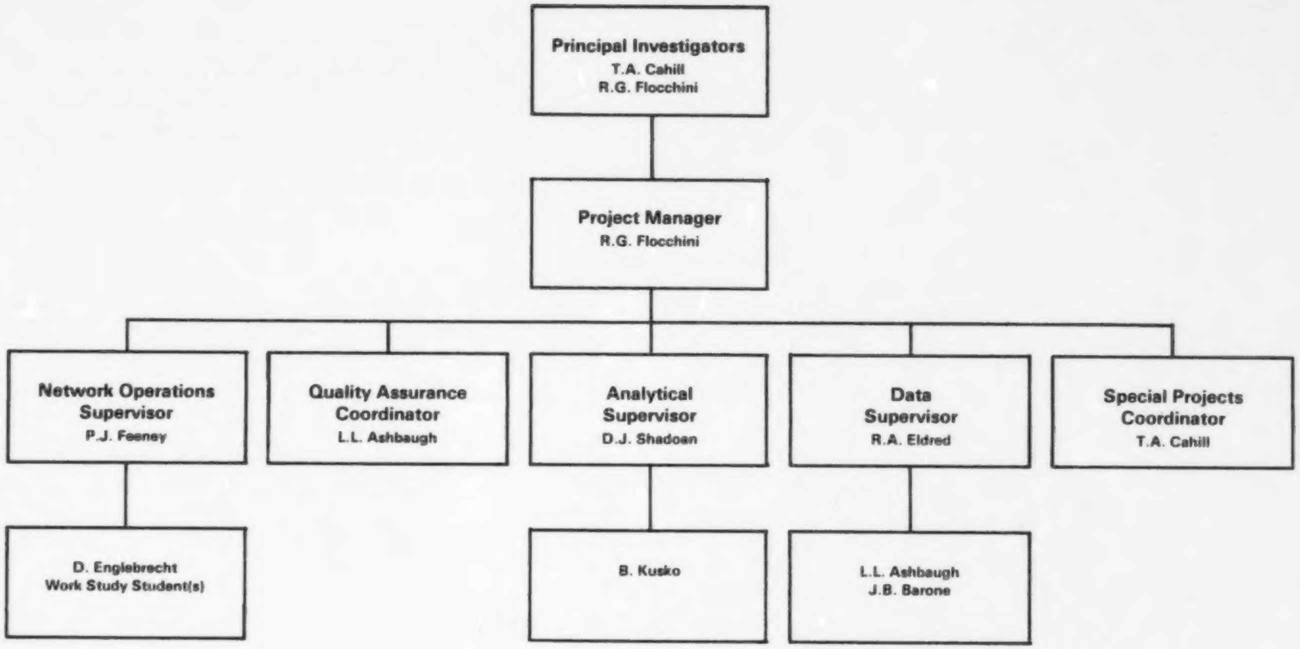
Principal Investigators
T.A. Cahill
R.G. Flocchini
Project Manager
R.G. Flocchini
Network Operations Supervisor
P.J. Feeney
Quality Assurance Coordinator
L.L. Ashbaugh
Analytical Supervisor
D.J. Shadoan
Data Supervisor
R.A. Eldred
Special Projects Coordinator
T.A. Cahill
D. Englebrecht
Work Study Student(s)
B. Kusko
L.L. Ashbaugh
J.B. Barone

Figure A-1. Organization chart.

5. Evaluates flow readings prior to entering into the analytical system for conversion constants to ng/m^3.

6. Supervises all gravimetric analyses.

7. Coordinates quality assurance field experiments, working with the Quality Assurance Coodinator and Special Projects Supervisor.

8. Oversees sample retrieval and storage after analyses.

9. Prepares Network Report every three months.

10. Maintains records on equipment changes and maintenance, down-time, voided samples.

III. QUALITY ASSURANCE COORDINATOR

A. Basic Function:

The Quality Assurance Coordinator is responsible for the conduct of the quality assurance program and for taking or recommending measures.

B. Responsibilities and Authorities:

1. Develops and carries out quality control programs, including statistical procedures and techniques, which will help agencies meet authorized quality standards at minimum cost.

2. Monitors quality assurance activities of the group to determine conformance with policy and procedures and with sound practice; and makes recommendations for correction and improvement as may be necessary.

3. Seeks out and evaluates new ideas and current developments in the field of quality assurance and recommends for their application wherever advisable.

4. Advises management in reviewing technology, methods, and equipment, with respect to quality assurance aspects.

5. Coordinates schedules for measurement system functional check calibrations, and other checking procedures.

6. Evaluates data quality and maintains records on related quality control charts, calibration records, and other pertinent information.

7. Coordinates and/or conducts quality-problem investigations. Interfaces with the external quality assurance program.

IV. ANALYTICAL SUPERVISOR

A. Basic Function:

The analytical supervisor (AS) is responsible for the elemental analysis of all samples associated with the EPA grant. Since the duties of the AS correspond to those of the director of Analytical Services, it is desirable that the two positions be held by the same person.

B. Responsibilities and Authorities:

1. Maintains the PIXE system, prepares the system for analysis prior to each cyclotron run, and is responsible for preparing a schedule for the run.
2. Maintains a logbook of procedures for pre-run set up, for sample analysis, and for post-run shutdown.
3. Obtains the written log of flow rates and gravimetric masses for the SFU's and VI's from the appropriate Network supervisor and prepares a computer log. Prepares run sheets and tray files.
4. Prepares a special reanalysis tray to be run before and after the network samples. The AS shall certify the accuracy of the system before any samples are analyzed. Submits periodical reports on the quality assurance of the analysis system.
5. Validates the results of all analyses and stores the collated concentrations on magnetic tape for use by the Data Supervisor. Is responsible for the computer reanalysis of samples which were incorrectly analyzed during the run.
6. Maintains the computer programs for data acquisition, for the analysis of sample and standard foil spectra, and for the manipulation of the files of collated concentrations. Maintains a notebook describing the programs and how they are used.

V. DATA SUPERVISOR

A. Basic Function:

The Data Supervisor (DS) is responsible for the analysis of the network data delivered by the Analytical Supervisor.

B. Responsibilties and Authorities:

1. The DS maintains the following libraries:
   a. All network SFU data by time period;
   b. All particle data by site;
   c. All special samples;

    d. All appropriate meteorological parameters. (Magnetic Tape from Library (b) shall be sent to EPA/LV).

2. Isolates anomolous results, and decides, with the cooperation of the Analytic Supervisor, which samples need to be reanalyzed.
3. Prepares standard data summaries for each site and for the entire network.
4. Prepares periodic comparisons of the data of coincident samples.
5. Is responsible for characterizing the particulate concentrations by site and season. Also is responsible for statistical programs to investigate special effects.
6. Is responsible for the production of appropriate maps and plots.
7. Is responsible for investigating the relationship between the particulate concentrations and appropriate meteorological parameters. Also is responsible for studies of visibility reduction at the major sites.
8. Maintains a notebook describing the analysis programs and how they are used.

VI. SPECIAL PROJECTS COORDINATOR

A. Basic Function:

The Special Projects Coordinator is responsible for all air sampling and sample reduction programs not associated with network operations.

B. Responsibilities and Authorities;

1. Coordinates all special projects involving non-network air sampling, analyses of materials, etc., with the EPA project supervisor.
2. Oversees all special project operations in cooperation with the Network Supervisor (when the network is involved) and the Quality Assurance Coordinator.
3. Oversees preparation of samples for analysis, including flow rate calibrations, mass values, etc., prior to transmittal to the Analytical Supervisor.
4. Coordinates data reduction with Data Reduction Supervisor.
5. Prepares documentation of all special projects, prior to publication.

APPENDIX B

NONSTANDARD AIR SAMPLERS

In the course of this study, a number of other instruments were used for a variety of purposes: Sierra Multiday impactors provided daily (24-hour) data at Zion, Bryce, and Canyonlands National Parks, supported the VISTTA study, and aided in sampler intercomparisons. The additional cutpoint at 0.5 µm greatly aids studies of visibility, and several publications have appeared with these data. Virtual impactors were used solely for sampler intercomparison. Intercomparison between the SFU and VI were done at UCD; Las Vegas, Nevada; Canyonlands National Park, Utah; Yellowstone National Park, Wyoming; Carlsbad Caverns National Park, New Mexico; and Cedar Mountain, Utah. Other virtual impactors were operated as part of the VISTTA study. Preliminary data were taken with Battelle 8-stage impactors, Florida State streakers, and a high sensitivity SFU, but findings from these are not included in this report.

SIERRA INSTRUMENTS MULTIDAY IMPACTOR

Particulate samples were collected at Yellowstone National Park, Wyoming; Canyonlands National Park, Utah; Zion National Park, Utah; and Cedar Mountain, Utah, in three size ranges (15 µm to 3.5 µm, 3.5 µm to .50 µm, and 0.50 µm to 0.01 µm) by Lundgren type rotating drum impactors. These devices use two impaction stages and a filtration stage. The rotary drum impaction surfaces were covered with 530 $\mu g/cm^2$ of type S mylar with a coating of approximately 65 $\mu g/cm^2$ of Apiezon L grease. The final filter used was a 0.4 µm pore size Nuclepore. The samplers were equipped with constant flow devices which maintained a flow rate of 20 lpm. This unit delivered daily samples suitable for optical, beta-gauge, and PIXE analyses. The use of this instrument is described in Flocchini (1976). Extensive studies describing particle loss, particle sizing, sample transport and handling are described in Cahill (1976).

VIRTUAL IMPACTOR

Virtual impactor (VI) samples were collected at Carlsbad Caverns, New Mexico; Cedar Mountain, Utah; Canyonlands National Park, Utah; and Yellowstone National Park, Wyoming, coincident with the network's SFU operation to provide a comparison of this studies data to that of other studies which use the VI sampler.

The VI selected was the Sierra Instruments Model 244 Dichotomous Sampler (Stevens 1975, 1978) (Loo 1975, 1979). This sampler collects two size fractionated samples (2.5 to 15 µm, and less than 2.5 µm), nominally the same as the SFU sampler. The two-particle fractions are collected on 37mm Teflon membrane filters. The flow-controlled pump maintains a 16.7 lpm flow rate within ±3% over a 0 to 40 cm Hg pressure drop across the fine-particle filter by maintaining a constant pressure differential across a valve on the inlet side of the vacuum pump.

The sampler's inlet is designed to have an upper particle cut-off diameter of approximately 15 µm. Particles smaller than 15 µm pass through a flow straightening tube and enter the virtual impactor head (Figure B-1). The aerosol then is accelerated through the impactor jet. By virtue of their greater inertia, particles larger than 2.5 µm impact into the "void" of the receiver tube, and are then collected on a 37mm filter. Since ten percent of the flow passes to the coarse stage, ten percent of the fine particles are also collected on this filter. The remainder of the fine particle laden air passes around the receiver tube end and is collected on a second 37mm filter at a flow rate of 15.0 lpm.

Table B-1 summarizes a comparison study using SFU, VI and a low-volume open face filter samplers performed at UCD. The arithmetic mean and standard deviation of ratios of results from the three types of samplers are shown. For coarse soil type particles (Si, K, Ca, Fe), the average ratio was 0.93 (VI/SFU). The ratio was 0.94 for the sum. For sulfur, the ratio was 1.16 (VI/SFU).

Other VI/SFU comparison studies have been conducted. The major EPA/DOE study referred to in the body of this report included several VI's (units D,R,C,L, and S in Figure B-2). The original paper describing the development of SFU's by the EPA-Research Triangle Park (Parker et al. 1977) included a VI comparison with good agreement, as did a study at Los Alamos (Ferek et al. 1977). Tables B-2 and B-3 summarize the agreememt between SFU and VI samplers from these studies, none of which, incidently, used the coated filters (designed to inhibit the problem of solid particle bounce) now used on all units.

The first large scale SFU/VI intercomparison in field conditions was in the Willamette Valley study done by the Oregon Dept. of Environmental Quality, June-November 1978. Results for sulfur are shown in Figure B-3 corresponding to a correlation coefficient of 0.82 and a slope of 1.08 ± 0.12. The corresponding values for fine iron, a soil-derived particle, are 0.78 correlation coefficient and a slope of 0.97 ± 0.12, showing the value of coated filters in field conditions. With the development at UCD of a capability to measure accurate small mass values gravimetrically, a study was done near Las Vegas on fine mass levels. The results gave an SFU/VI relationship: SFU = 0.917 VI + 1.0 µg/m^3.

The co-location of VI with SFU sampler produced a modest data set for comparing the results of these systems. Though most of the possible samples to be collected by the VI were either not collected or invalidated due to instrument malfunction, a significant data set for comparing the VI and SFU remained. The resulting comparison set consists of 158 sample periods: 0 from Carlsbad Caverns National Park, 36 from Canyonlands National Park, 47 from Cedar Mountain and 75 from Yellowstone National Park. The operational problems of the VI resulted largely from the lack of highly trained field operators to promptly identify the subtle problems associated with this relatively complex sampler, the lower priority for repairs and for preliminary data screening for the VI samplers compared with the SFU and the length of time required for repairs (most repairs were not performed in the field).

The average concentrations measured by the two samplers were generally in

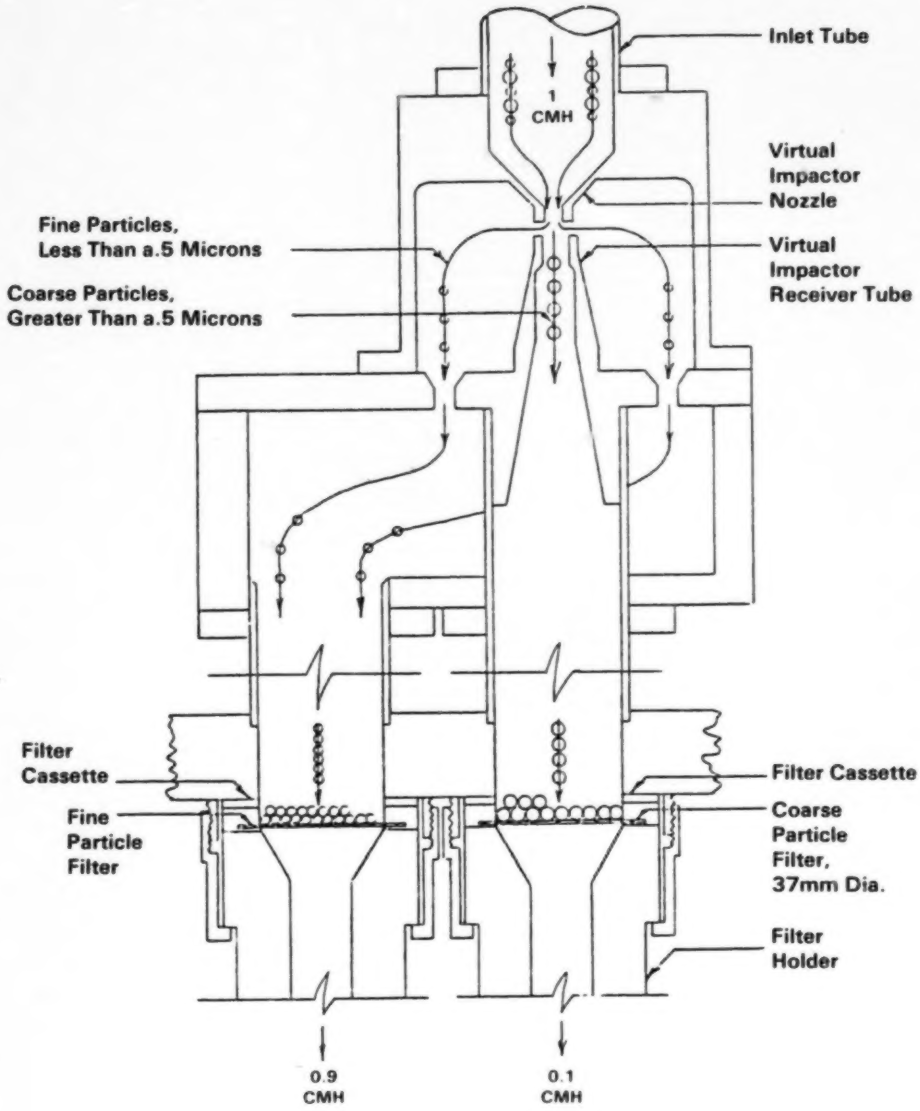
Inlet Tube
1 CMH
Virtual Impactor Nozzle
Fine Particles, Less Than a.5 Microns
Virtual Impactor Receiver Tube
Coarse Particles, Greater Than a.5 Microns
Filter Cassette
Filter Cassette
Fine Particle Filter
Coarse Particle Filter, 37mm Dia.
Filter Holder
0.9 CMH
0.1 CMH

Figure B-1. Virtual impactor particle sizing mechanism.

TABLE B-1. COMPARISON OF VIRTUAL IMPACTOR AND STACKED FILTER UNIT

	VI/SFU	VI/Total Filter	SFU/Total Filter
Si:			
Coarse	0.91 ± 0.11		
Fine	0.68 ± 0.25		
Sum	0.91 ± 0.10	0.84 ± 0.10	0.91 ± 0.11
K:			
Coarse	0.90 ± 0.12		
Fine	1.08 ± 0.09		
Sum	0.92 ± 0.11	1.01 ± 0.25	1.07 ± 0.28
Ca:			
Coarse	0.87 ± 0.12		
Fine	0.88 ± 0.12		
Sum	0.84 ± 0.15	0.80 ± 0.28	0.97 ± 0.32
Fe:			
Coarse	1.02 ± 0.15		
Fine	0.59 ± 0.07		
Sum	1.20 ± 0.45	1.09 ± 0.34	1.00 ± 0.41
Pb:			
*Coarse	0.40 ± 0.04		
Fine	1.16 ± 0.21		
*Sum	0.86 ± 0.11	0.69 ± 0.14	0.75 ± 0.33
S:			
*Coarse	0.40 ± 0.04		
Fine	1.16 ± 0.21		
*Sum	0.86 ± 0.11	0.96 ± 0.05	1.06 ± 0.21
Total Mass:			
Coarse	0.83 ± 0.16		
Fine	1.23 ± 0.13		
Sum	0.93 ± 0.14		

*Based on Two Samples

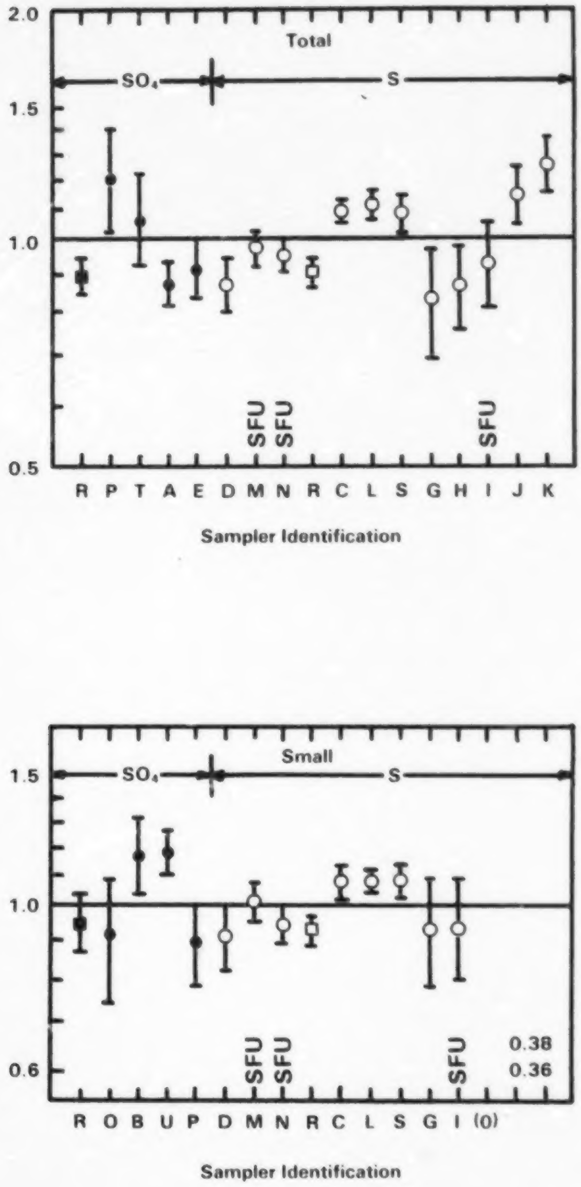

Figure B-2. Sulfur/sulfate results from Charleston study.

TABLE B-2. COMPARISONS OF PARTICLE COLLECTION EFFICIENCY - ALL SIZES SUMMED

Reference	Site	Samplers Compared	Ratio of Observed Masses			
			Soils	Sulfur	Lead	Mass
Parker et al	Durham	SFU/VI	0.78	1.07	1.00	-
Ferek et al	Los Alamos	SFU/VI	1.30	0.85	0.85	-
Camp et al	Charleston	SFU/Mean	0.87± 0.17	0.94± 0.02	0.94± 0.04	0.95± 0.14*
		SFU/Median	0.89	1.01	0.97	0.98
Cahill et al	Davis	SFU/TF	1.06	1.01	0.90	0.99

* = Sum of Elements
TF = Total Filter

TABLE B-3. COMPARISONS OF PARTICLE SIZING EFFICIENCY, SFU vs. VI. FRACTION OF MASS ON FINE STAGE

Site	Year	Samplers	Soil	Sulfur	Lead	Reference
Durham	1967	SFU: (12µm, 12.7 cm/s)*	0.11	0.74	0.68	Parker et al (1977)
		VI	0.12	0.83	0.74	
Los Alamos	1976	SFU: (8µm, 7.4 cm/s)	0.13	0.83	0.75	Ferek et al (1978)
		VI	0.15	0.90	0.83	
Charleston	1977	SFU: (12µm, 12.7 cm/s and 8µm, 7.4 cm/s)	0.25**	0.92	0.81	Camp et al (1978)
		VI:	0.10	0.89	0.76	

*Nuclepore filter pore size, face velocity
**UCD SFU (8 µm, 7.4 cm/s) - 0.15

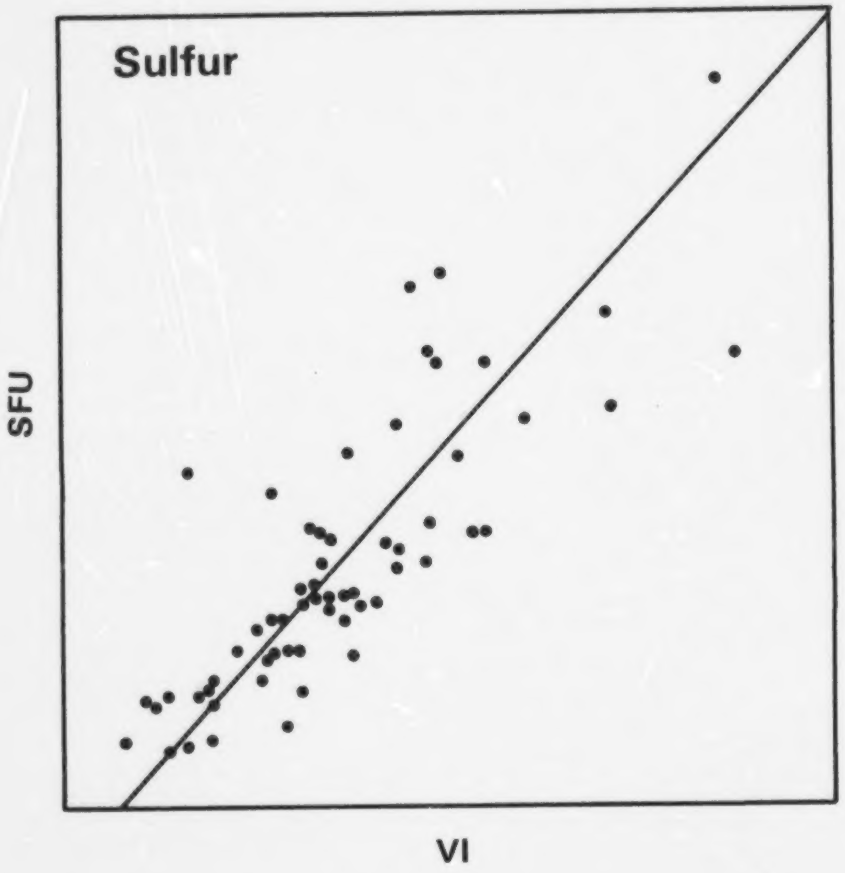

Figure B-3. Scattergram comparison of stacked filter unit and virtual impactor fine sulfur.

good agreement. Table B-4 compares the arithmetic mean concentrations of selected elements and mass for the three locations. For the coarse particles, the SFU mean concentrations are about 15% larger than the VI concentration. For fine sulfur and fine mass, the SFU levels are about 20% and 10% larger, respectively.

TABLE B-4. STACKED FILTER UNIT AND VIRTUAL IMPACTOR CONCENTRATIONS. (ng/m^3)

		Canyonlands			Cedar Mountain			Yellowstone		
		SFU	VI	$\frac{SFU}{VI}$	SFU	VI	$\frac{SFU}{VI}$	SFU	VI	$\frac{SFU}{VI}$
Coarse	Si	859	828	1.04	587	481	1.22	360	254	1.42
	Al	221	207	1.07	151	138	1.09	91	52	1.75
	K	147	139	1.06	58	50	1.16	43	39	1.10
	Ca	292	272	1.07	216	216	1.00	72	67	1.07
	Fe	147	135	1.09	79	88	0.90	54	46	1.17
	mass	5597	5722	0.98	3643	3497	1.05	2221	1581	1.40
Fine	S	310	307	1.01	315	230	1.37	113	89	1.27
	K	76	69	1.10	25	21	1.19	20	20	1.00
	Ca	82	45	1.82	41	27	1.52	19	23	0.83
	Fe	50	28	1.79	26	17	1.53	15	9	1.67
	mass	3353	4747	0.70	2966	2430	1.22	1627	1268	1.29

For fine soils, the SFU values are around 50% larger.

The VI also verified the measurements of relative composition by the SFU. For example, the soil elements on each sampler were highly intercorrelated and the ratios of the elements for the two samplers were virtually identical. The VI also verified the coarse soil to coarse mass ratio measured throughout the network. At all six samplers in the comparison, the sum of the coarse soil elements with their associated oxide accounted for about half of the coarse mass. The relative composition of the fine particles was also similar. The ratio of fine sulfur to fine mass were similar at each site (0.07 and 0.09 at Canyonlands, 0.11 at Cedar Mountain and 0.07 and 0.08 at Yellowstone). At Cedar Mountain, the correlation between fine mass and fine sulfur was nearly the same for each sampler (0.70). The correlations were lower at Canyonlands and Yellowstone, though marginally higher on the SFU's than on the VI's.

While the mean values for sulfur and other elements seen by SFU's and VI's in the field are reasonably close the correlation coefficients and intersite variations are disappointing. Problems were encountered siting virtual impactors at some locations, and mechanical problems resulted in less than 50% of all possible samples being received. Since the units were able to operate only towards the end of the program, quality assurance protocols were still being modified for the VI's when sampling ended in September, 1981. The VI filters were uncoated and serious sample loss in transport was documented. Photographic evidence was obtained of nonuniform deposits on the coarse particle VI stage, perhaps caused by the movement of loose sample material. Thus, the fact that SFU's saw more mass than VI's is not suprising.

SPECIAL STUDIES

In addition to the routine operation of the network several special studies were conducted to get detailed information on particle size and chemical composition. The first involved cooperation with the VISTTA study in June-July 1979 at Zilnez Mesa. Manual (early model) SFU's and multiday impactors were operated side by side with automated (Beckman) virtual impactors run in a manual mode, Cal Tech low pressure impactors, electrical mobility analyzers, nephelometers, and other instruments. There was excellent agreement between diverse instruments as shown in Figures 3 and 4 of Macias et al. (1981a). Some of the results of the UCD work are shown in Table B-5. Despite differences in flow rate (5 lpm to 20 lpm for the SFU's), sampler intakes (with and without decclerators), and integration periods (one to three days), good agreement was observed for fine particles. Typical agreement for sulfur was within 5%. Even more impressive was the ±3% agreement between one- and two-day SFU's for gravimetric mass, since the fine mass averaged only about 5 $\mu g/m^3$ and the coarse mass about 12 $\mu g/m^3$.

TABLE B-5. VISTTA DATA - ZILNEZ MESA

SULFUR (ng/m^3)

	Multiday Impactor[a]				Stacked Filter unit[b]		
Date	Stage 1	Stage 2	Stage 3	Sum	Coarse	Fine	Sum*
6/26	6	37	152	195			
6/27	9	54	155	218			
6/28	4	65	715	784	23	447	470**
6/29	47	147	827	1021	38	792	830**
7/02	5	63	396	464	55	432	487
7/03	6	50	185	242	51	195	246
7/04	4	69	226	299			
7/05	5	43	304	352			
7/06	4	24	127	156			
7/07	6	24	175	206			
7/08	8	49	204	261			
7/09	13	18	183	213			
7/10	12	26	223	260			
7/11	19	25	325	370	60	312	372

[a] Stage 1 - 15 μm to 3.6 μm; Stage 2 - 3.6μm to 0.65 μm; Stage 3 - less than 0.65 μm D

[b] 1 day SFU's only run on these 5 days; cut at 2.5 μm

*1-day SFU's ratio to Multiday is 0.97 ± 0.11. SFU were also run for 2- and

3-day durations giving ratios to the Multiday of 1.04 ± 0.06 and 0.97 ± 0.14 repectively.

**Time periods not identical to Multiday; off by 10 hrs.

APPENDIX C

QUALITY ASSURANCE PROCEDURES

INTERNAL QUALITY ASSURANCE

Sample Handling

When filters were received from Nuclepore Corporation, they were first checked to see that they were as ordered. If not, they were not used and replacements were obtained. No further checks were made until exposed filters were returned from the field.

When filters were received from the field, the sample log sheet was reviewed for gross errors. The sample dates and elapsed time were checked for consistency. If not consistent, and no explanatory note was received, the operator was telephoned to resolve the problem. If it was not resolvable, the sample was placed in a "dead file" called Tray X for storage. The samples in Tray X were never used for network purposes, but were stored in case they were needed for special purposes. The flow rates were checked next. If the end flow rate was less than 7 lpm, the sample was placed in Tray X. If the elapsed time was less than 1,000 minutes or greater than 10,000 minutes, the sample was placed in Tray X. Further elapsed time checks were made during computer processing of data. If any note was received from the operator describing a problem with the sample, the problem was resolved or the sample was placed in Tray X.

The filters were checked next. If a filter was torn upon receipt, neither stage was used, but both were placed in Tray X. If a filter had a fingerprint, only that filter was placed in Tray X. If the holder grid was installed upside down, a note was made to mount the sample with the wide bars oriented perpendicular to the beam. If the filter was torn during weighing, it was salvaged, if possible.

The data was again reviewed when the filter weights were recorded in the sample weight logs. If two sets of data existed for the same filter number, the electrobalance printed record and shipping dates were examined to differentiate the two. The second set was marked by a prime (') on the filter number. If the sample weight was very small or negative, the balance printer record was examined for transcription errors, and records for other sites and sample periods near the affected one were examined for errors or inconsistencies. If any problems were found, they were resolved or the affected samples were placed in Tray X. Before an analysis run, all trays were checked against the sample weight log for consistency.

Computer Log and Run Sheets

After all entries for a given month were made in the sample weight log and checked, a computer log was prepared. Entries in the computer log followed those in the weight log closely. Each entry listed the start date, elapsed time, initial and final rotameter readings and coarse and fine masses. (Only the differences between post- and pre-weight were entered). Masses less than 10 μgm were entered as 10 μgm. If a coarse stage was missing, and a fine stage was present, a zero coarse mass was entered. All entries in the computer log were checked with those in the weight log. Gross typing errors were usually identified by misaligned columns.

A printout was made using a specially written computer program. This included the original entries plus calculated parameters. Sample duration was printed: if it ran more than 48 hours beyond the normal 72-hour duration an error message was printed. The flow rates in liters per minute were corrected for altitude and rotameter bias. The printout listed the conversion constant (cm^2/m^3) and the coarse and fine masses in μg/m. The printout was reviewed for anomalous data (unusual run times, conversion constants, masses etc.).

Run sheets to accompany the PIXE analysis were also prepared by computer. These indicated which positions in the trays had valid samples. In order to check that every sample had an entry in the run sheet, all empty positions in the trays were compared to corresponding blanks on the run sheets. The actual instructions to tell the analysis program which slides to analyze were contained in files which were typed in using these computer generated run sheets. This was generally a simple task since only missing samples needed to be identified. After the entries in this file were checked, a note was made on the run sheet.

PIXE Analysis

Selected elemental foils were analyzed at the start of each cyclotron run. These standards verified that the analysis system was working properly and provided a normalization constant to account for changes in beam energy, charge collection and detector solid angle.

Before the network samples were analyzed a reanalysis tray of SFU samples was run. The concentrations obtained were compared to previously measured values. If they were predominantly within 10-15% of the past values, the run proceeded. If there was a bias, then the elemental foils were rerun. Any problems were identified and corrected before the run proceeded.

Throughout the run the operators periodically checked the analyses to verify that no problems occurred. The analysis program printed special messages of problems: low charge (below 750 nanocoulombs), bad blank subtraction or no peaks found (indicating a bad sample), and unidentified peaks (usually denoting energy miscalibration). When these messages occurred the operator isolated the problem, often rerunning the sample. The operator commented on these problems on the run sheet.

At the end of the network samples the reanalysis tray was run again. If these values disagreed with the pre-run values, then selected samples throughout the run were reanalyzed to determine when the problems began. If necessary, a portion of the samples were reanalyzed.

Post Analysis Procedures

At the end of the network analysis, but before the cyclotron was shut down, the analysis supervisor reviewed the PIXE run sheets and the PIXE analysis printout log. If any analyses were missing or irretrievably bad, the samples were reanalyzed at that time. Spectra needing to be reanalyzed via the computer were noted.

The elemental masses for each run were collated into summary files by the analysis program. These files were printed and reviewed. Samples in which key elements were missing or in which amounts were abnormally large or small were noted. For the coarse stage, the key elements were silicon, calcium and iron, while for the fine stage it was sulfur. These spectra, along with those noted from the previous paragraph, were reanalyzed with the computer to validate the results. If problems in the spectrum were suspected, the sample was reanalyzed.

EXTERNAL QUALITY ASSURANCE PROTOCOLS

Rockwell International Environmental Monitoring and Service Center under contract to EPA conducted a program of external audits on the operation of this network. The program consisted of:

- weight audits
- flow audits
- field audits
- filter analysis system audit
- system audit

Weight Audits

The purpose of the weighing audit was to evaluate the accuracy of the UCD filter weighing procedure and weighing equipment. There were seven such audits from July 1980 to April 1982.

At Rockwell a set of six aluminum weights (3 pair) was used to perform the audit. Each weight was altered by filing away some of the mass so that the weight difference between a pair of weights would simulate the particular loading of a typical filter sample. The exact weight of each mass prior to shipping was determined by performing three weighings conducted on three separate days and averaging the results. The weighings were done on a Cahn Model 26 Electrobalance which had been calibrated with NBS traceable, Class M weights.

The set of weights was then sent to UCD together with instructions and a data sheet. UCD personnel were instructed to weigh each mass using the same procedures used for filter weighings. To perform the weighings, UCD used a Cahn Model 25 Electrobalance calibrated with NBS traceable, Class M weights.

The masses and the completed data sheet were then returned to Rockwell.

The masses were then reweighed on the Cahn Electrobalance to insure that no significant change had occurred during transit. This was done by weighing each mass three times, on three separate days. If no significant change was found, the "official" Rockwell weight of each mass would be the average of six weighings. A comparison between Rockwell and UCD values was then made. Two comparisons of the data were made. One compared the weights of the individual masses obtained by Rockwell and those obtained by UCD. The other was a comparison of the weight differences between pairs of masses. All the weight audits resulted in good agreement between Rockwell and UCD. An example of a typical weight audit (August 1981) is shown in Table C-1.

Flow Audits

For the purpose of conducting flow rate performance audits of all the SFU's, Rockwell sent calibrated orifice flow measuring devices together with audit procedures to the sampler operators in the field. The device was attached to the inlet of the SFU allowing the entire sample flow to pass through the orifice. The pressure drop across the orifice, measured in inches of water with the magnehelic gauge, was recorded and used to calculate audit flow. The audit flow was then compared to the flow as indicated by the sampler's rotameter which was calculated by Rockwell using the calibration curves provided by UCD.

Table C-2 show the results of the audits for August 1980 to August 1981, respectively. The site flow values in parenthesis represent flows modified by a temperature correction not used by UCD except for extreme temperatures. The audit flow values in parenthesis represent flows assuming the site operator misread the magnehelic gauge (e.g., 0.19 instead of 1.19 inches of water). Misreading of the gauge was eliminated in subsequent audits by having the operator draw the position of the needle on an illustration of the gauge face. The values in parenthesis in the percent difference column is appropriate assuming the parenthetic flow value is correct.

Field Audits

In addition to the flow audits, on-site field audits were performed by Rockwell at selected sites. The purpose of the audits was to assess the performance of the personnel and equipment and to provide technical assistance as required, in order to control and improve the quality of the data. The system audits involved interviews with personnel and a visit to the sampling site in order to evaluate the following elements of the program: organization and staffing, training, site selection, equipment, procedures, maintenance, documentation and communication. Field audits were performed in the fall of 1980 and the fall of 1981. In general Rockwell reported a satisfactory field operation though they did make recommendations having to do with improved or better documented operator procedures and communications between the field and UCD.

TABLE C-1. WEIGHT AUDIT RESULTS (mg)

Mass No.	Rockwell		UCD		Difference*	
	Mass	Mass Difference	Mass	Mass Difference	Mass	Mass Difference
1	9.950	0.894	9.956	0.894	0.006	0.000
2	10.844		10.850		0.006	
3	13.089	0.573	13.095	0.572	0.006	0.001
4	12.516		12.523		0.007	
5	17.951	0.707	17.955	0.708	0.004	0.001
6	17.244		17.247		0.003	

*Difference = Davis - Rockwell

TABLE C-2. FLOW AUDIT RESULTS

Site No.	Site flow (lpm)	Audit Flow (lpm)	% Diff.*
1	12.5	11.6	7.8
*2	10.3	4.9 (9.7)**	110.0 (-1.0)
3	9.0	9.3	-3.2
4	10.4	12.5	-16.8
5	10.1	11.1	-9.0
6	10.3	11.9	-13.0
7	9.4	12.6	-25.0
8	10.2	11.7	-12.8
9	10.1	11.3	-10.6
10	9.6	12.1	-20.7
11	10.5	11.1	-5.4
12	Invalid	Invalid	Invalid
13	11.5	11.9	-3.4
14	9.8	8.8	11.4
*15	11.1	4.2 (10.1)	164.0 (9.9)
*16	10.2 (9.5)	8.9	14.6 (6.7)
*17	11.9 (11.2)	11.2	6.3 (0)
*18	8.8	5.9 (10.9)	49.2 (19.0)
19	11.8	11.1	6.3
20	9.7	11.2	-13.4
*21	10.9	4.5 (9.4)	142.0 (16.0)
*22	10.7 (10.1)	9.0	18.9 (12.2)
23	10.7	12.4	-13.7
24	11.2	10.4	7.7
25	10.7	11.3	-5.3
26	10.6	8.0	32.5
27	8.6	10.4	-17.3
28	10.7	11.6	-7.8
29	8.6	10.9	-21.1
30	9.0	9.5	-5.3
31	11.0	11.5	-4.3
*32	12.1	4.2 (10.3)	188.0 (17.5)
33	10.7	9.0	18.9
34	11.1	11.7	-5.1
35	11.4	12.7	-10.2
36	9.0	7.5	+20.0
37	10.5	10.8	-2.8
38	10.9	11.2	-2.7
39	9.3	10.4	-10.6
40	12.3	12.2	0.8
Mean ± Standard Deviation			0.9 ± 13.3

$$^{*}\%\ \text{Difference} = \frac{\text{Site flow - Audit Flow}}{\text{Audit Flow}} \times 100$$

**Parenthetic values are explained in the text.

Filter Analysis System Audit

Four filter analysis audits were done between fall 1980 and spring 1982. In the first, 24 identical audit samples were sent to UCD as a check of internal precision while in the remaining audits equivalent samples were sent to UCD and the NEA Research Laboratories, Beaverton, Oregon, for XRF analysis. The results of the first and second audits are summarized in Table C-3 and Figure C-1 respectively. Subsequent audits produced similar results. Rockwell concluded that "The UCD PIXE technique is fundamentally sound and is capable of measuring elemental concentration on particulate filters."

System Audits

Rockwell representatives visited UCD in May of 1980 and 1982. The purpose of these visits was to examine the UCD facilities and evaluate the performance in carrying out the Western Particulate Characterization Study. Overall, Rockwell found that "UCD is doing a very good job".

TABLE C-3. ELEMENTAL ANALYSIS AUDIT RESULTS, 21 SAMPLES ANALYZED

Element	Mean ($\mu g/m^3$)	Standard Deviation ($\mu g/m^3$)	Percent Standard Deviation (%)
Cu	46.47	3.28	7.06
S	22.19	1.83	8.25
Al	44.44	3.79	8.54
Ca	45.67	3.57	7.81
Ni	36.28	2.74	7.56
Fe	42.93	3.23	7.51
Mn	36.54	3.03	8.30
Cl	13.63	1.33	9.72
K	49.53	4.00	8.08
Br	22.56	1.61	7.13

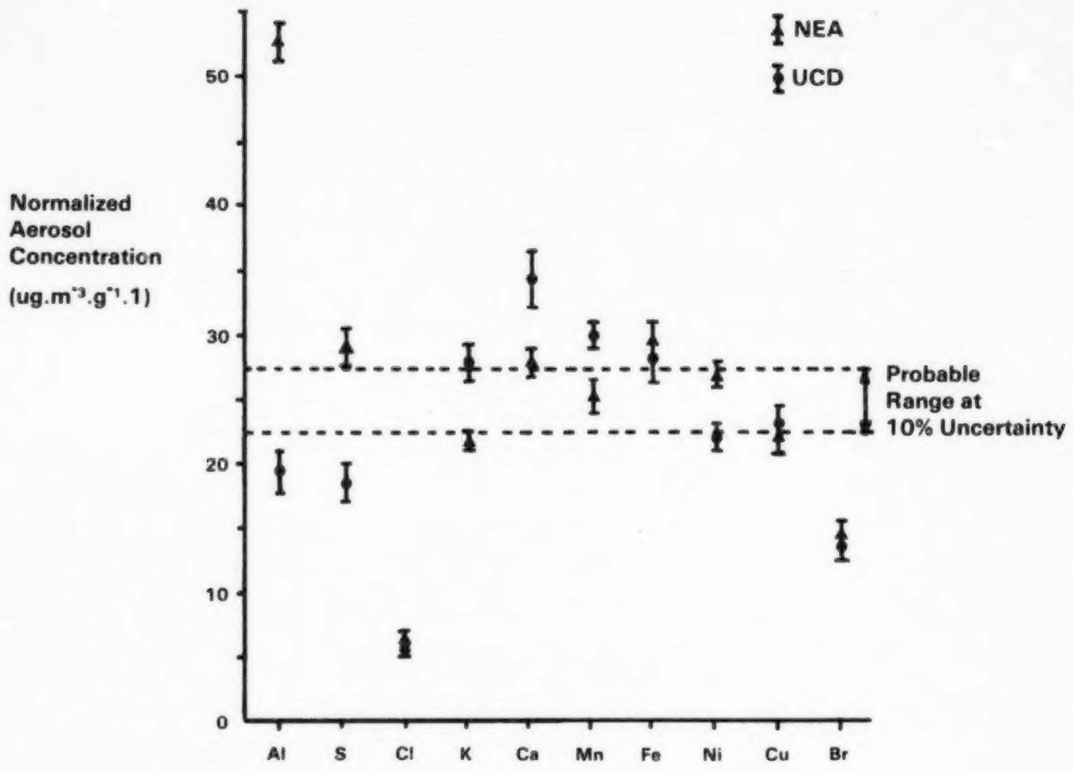

Figure C-1. Comparison of elemental analysis. Mean and standard deviation shown for eight samples. Results normalized to typical aerosol concentration.